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HAND-BOOK

OF

MINERAL ANALYSIS.

BY

FRIEDRICH WÖHLER,
PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF GÖTTINGEN.

EDITED BY

HENRY B. NASON,
PROFESSOR OF CHEMISTRY IN THE RENSSELAER POLYTECHNIC INSTITUTE,
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PREFACE TO THE AMERICAN EDITION.

The present edition of Wöhler's Hand-Book of Mineral Analysis is a translation of the last German with some changes and additions.

A few of the methods here described might have been omitted, and newer, in some cases preferable ones, given instead, but it has been thought advisable to present the book in nearly the same form as the original.

Free use has been made of the excellent translation of the first edition by Dr. A. W. Hoffman, and frequent reference had to the French edition by Messrs. Grandeau and Troost, from which many of the illustrations of apparatus have been taken.

The work is not intended to take the place of larger and more complete works on analysis, but it is believed that it will be found a convenient companion to these in the laboratory.

H. B. N.

Troy, N. Y., Dec. 15, 1870.

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PREFACE.

THIS collection of examples for illustrating the most important processes for determining the composition of mineral substances, is designed chiefly for use in the laboratory.

It is drawn up under the impression that it is easier for most minds to obtain a clear insight into general relations and laws by the study of special cases, than, inversely, to acquire a knowledge of individual cases by first directing the attention to general rules. An endeavor has been made to arrange the book in such a manner as still to leave enough to demand the reflection of the student and the explanations of the teacher; the latter also must point out the authority for the individual methods here given, and also which he considers the best.

FRIEDRICH WÖHLER.

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HANDBOOK

OF

MINERAL ANALYSIS.

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1. CHLORIDE OF SODIUM.

$NaCl$.

PERFECTLY pure crystallized common salt is strongly heated, to expel adhering moisture, weighed, dissolved in water, the solution slightly acidified with nitric acid, heated, and the chlorine precipitated by nitrate of silver, the liquid being at the same time violently agitated by stirring. When the chloride of silver has completely separated, leaving the liquid clear, it is filtered off and washed (with as little exposure to light as possible), first with hot water acidified with nitric acid, in order that it may not pass through the filter and subsequently with pure water. When the precipitate has been perfectly dried it is removed as completely as possible from the filter, and fused, in a weighed porcelain crucible, over the gas-lamp. The filter is completely incinerated by itself; the ashes are placed upon the cooled chloride of silver, and heated, first with a little nitric acid, in order to oxidize the reduced silver, and afterwards with a few drops of hydrochloric acid; the excess of acid having been expelled, the chloride of silver is again heated to fusion, allowed to cool, and weighed. 100 parts of AgCl contain 24.73 chlorine (and 75.27 silver).

The liquid in which the chloride of silver floats can also be decanted with care on a filter. The chloride can be collected in a weighed porcelain crucible, after washing, dried, gently calcined, and weighed. The chloride of silver being a little volatile, there is danger of loss if it is heated to fusion. The filter is burned by itself and the ashes weighed with the calcined chloride.

For the determination of the sodium, another weighed portion of chloride of sodium is carefully moistened, in a weighed platinum crucible, with concentrated sulphuric acid; after some time, a gentle heat is applied until all the chlorine has been expelled in the form of hydrochloric acid, when the excess of sulphuric acid is carefully evaporated, and the residual sulphate of soda finally heated to redness, a fragment of carbonate of ammonia being placed in the crucible, to decompose any acid salt. From the weight of the sulphate of soda, that of the sodium is calculated.

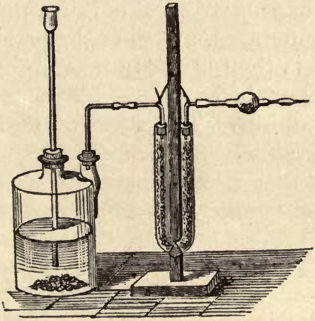
2. CHLORIDE OF SILVER.

AgCl.

In order to determine the composition of chloride of silver, a weighed quantity of pure silver is dissolved in dilute nitric acid, the solution precipitated with dilute hydrochloric acid, and the precipitated chloride of silver treated as in No. 1.

Or a weighed portion of fused chloride of silver may be heated with a low flame, in a bulb-tube, through

Fig. 1.



which a stream of hydrogen is passed until it is completely reduced to metallic silver, which is then weighed.

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3. SULPHATE OF SODA.

$NaO, SO_3 + 10\ HO.$

For the determination of the water, a weighed quantity of the salt is gradually and carefully heated in a platinum crucible, until the whole of the water is expelled, to insure which the heat is finally raised to ignition.

The sulphuric acid is determined by dissolving the salt in water and precipitating with chloride of barium. The liquid is then warmed, and must not be filtered until the sulphate of baryta has completely separated. The clear liquid is then poured upon the filter, without the precipitate, which is stirred up with hot water, again allowed to subside, the clear liquid being poured upon the filter, and the precipitate once more treated in the same way before it is thrown upon the filter, in order that none may pass through the pores of the paper. When perfectly washed, it is dried, separated as much as possible from the filter, the latter being completely incinerated, and its ashes added to the precipitate, which is then ignited and weighed. 100 parts of sulphate of baryta contain 34.29 of sulphuric acid, or 13.71 of sulphur. The amount of soda is determined by difference.

4. TARTRATE OF POTASSA AND SODA.*

Seignette-salt; Rochelle-salt, ($KO, NaO, \overline{T} + 8\ HO$).

The estimation of the water requires the cautious application of heat for a long period. The salt fuses even below 100°, and enters into ebullition at 120°, but does not lose the whole of its water till heated to 215°.

To determine the bases, the salt is ignited, the alkalies dissolved out of the carbonaceous mass by dilute hydrochloric acid, and the filtered solution evaporated to dryness; the mixed chlorides are heated to dull redness in a covered platinum crucible and weighed. They are then dissolved in a little water, and the solution mixed with a moderately concentrated solution of bichloride of platinum. The solution, with the suspended precipitate, is evaporated to dryness on the water-bath, the dry mass digested for some time with alcohol, and the potassio-chloride of platinum collected upon a filter which has been dried at 100°, and weighed. The filtrate, which contains the sodio-chloride of platinum, must still have a distinct yellow color. The platinum-salt is washed with alcohol, dried at 100°, and weighed. 100 parts correspond to 16.03 of potassium, or 19.33 of potassa.

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* Prepared by saturating a hot mixture of water and powdered tartar with carbonate of soda, filtering, and crystallizing.

The amount of the chloride of sodium may be ascertained by deducting the weight of the chloride of potassium from that of the mixed chlorides. It is safer, however, to control this result by direct determination, for which purpose the filtered liquid is carefully evaporated to dryness, and the mass strongly ignited in a covered platinum crucible; in order to insure the complete decomposition of the chloride of platinum, the ignition should be repeated, with addition of a few crystals of oxalic acid. From the cooled mass, the chloride of sodium is extracted with water.

When, as is frequently the case, the two alkalies are present as sulphates, together with an excess of acid, the greater portion of the latter is expelled by careful evaporation, and the saline mass afterwards ignited in a covered platinum crucible, into which small fragments of carbonate of ammonia are from time to time introduced. The joint weight of the neutral salts thus obtained is then determined.

In order to convert these sulphates into chlorides, the mass is moistened with water, mixed with pure chloride of ammonium, and heated in a covered crucible until the excess of the latter salt is expelled; this operation is repeated until the weight is constant, when the chlorides are separated by means of bichloride of platinum.

Or the solution of the sulphates may be precipitated by a solution of pure acetate of baryta, the precipitate filtered off, the filtrate evaporated to dryness, and the residue ignited. From the carbonized mass, water dissolves the alkalies as carbonates, which are converted into chlorides by treatment with hydrochloric acid.

5. SULPHATE OF SODA AND AMMONIA.*

$NaO, SO_3; NH_4O, SO_3+4HO.$

To determine the amount of soda, a weighed portion of the salt dried at 50° is gradually and carefully heated to redness in a platinum crucible, a fragment of carbonate of ammonia being held in the latter, at the end of the operation, to complete the removal of the excess of sulphuric acid. From the weight of sulphate of soda obtained, that of the soda is calculated.

The sulphuric acid is determined in another weighed portion of the salt, which is dissolved in warm water and precipitated by chloride of barium. From the weight of the sulphate of baryta, after filtering, washing and igniting, the amount of sulphuric acid is calculated.

The quantity of the ammonia may be estimated according to two different methods.

a. The weighed salt is dissolved in the smallest possible quantity of water, and the soluion mixed with excess of an alcoholic solution of bichloride of platinum, which precipitates the ammonia in the form of ammonio-chloride of platinum. When the precipitate is completely separated, it is filtered off, washed with alcohol, dried, and carefully ignited (*see* No. 1). From the weight of the residual platinum, that of the ammonia is calculated. 100 parts of platinum correspond to 26.37 of ammonia. In order to ascertain that the platinum does not contain any sulphate of soda or chloride of sodium which may have been precipitated by the alcohol, it is washed with water and again weighed.

---

* To prepare this salt, two equal portions of dilute sulphuric acid are taken, the one neutralized with carbonate of soda, then mixed with the other, ammonia added to neutralization, and the solution evaporated to the crystallizing point.

b. By distilling the weighed salt with a moderately concentrated solution of soda, the ammonia is evolved, and may be combined with hydrochloric acid. This is best effected in a small flask furnished with a funnel-tube by which the solution of soda is introduced, and a long condensing-tube, the end of which dips into moderately-strong hydrochloric acid. The liquid is retained in ebullition until one-half has distilled over. The hydrochloric solution is carefully evaporated to dryness in a weighed dish, over a water-bath, and the residue of chloride of ammonium weighed; or it may be converted into ammonio-chloride of platinum, which is then treated as above.

After determining the soda, the ammonia, and the sulphuric acid, the quantity of the water may be ascertained by difference. It may also be controlled by mixing a weighed portion of the powdered salt, in a platinum crucible, with an excess of freshly-burnt lime, free from water and carbonic acid; the mixture is covered with a layer of lime, the whole weighed, and very strongly ignited over a gas burner. The loss of weight represents the joint amount of the ammonia and water.

6. SULPHATE OF POTASSA AND MAGNESIA.*

$$KO, SO_3; MgO, SO_3 + 6 HO.$$

This salt loses all its water at 133°. The sulphuric acid is determined by precipitation by chloride of barium (*see* No. 3).

For the estimation of the magnesia, another weighed quantity of the salt is dissolved in water, mixed with chloride of ammonium, subsequently with ammonia, and the magnesia precipitated as phosphate of magnesia-ammonia by adding phosphate of soda. The precipitation is not complete till after the lapse of twelve hours, when the precipitate is collected on a filter and washed with a mixture of 3 parts of water and 1 part of caustic ammonia, in which it is perfectly insoluble. After drying, it is ignited, being thus converted into $2\ MgO, PO_5$ which contains 36.44 per cent. of magnesia. The potassa may be determined by difference. If a direct estimation be required, as is frequently the case, especially in the analysis of minerals, the salt is dissolved in water, and the sulphuric acid and magnesia precipitated by a hot saturated solution of hydrate of baryta. The excess of baryta is removed from the filtered liquid by adding a mixture of ammonia and carbonate of ammonia, the filtrate saturated with hydrochloric acid, evaporated, the chloride of potassium feebly ignited and weighed.

---

* This salt is easily obtained in crystals, by mixing a boiling saturated solution of 1 part of sulphate of potassa, with a saturated solution of 1½ part of sulphate of magnesia.

If both potassa and soda be present, they are separated as in No. 4.

From the mixed precipitate of magnesia and sulphate of baryta, the former is dissolved by diluted sulphuric acid, and afterwards precipitated and determined as above.

Another method consists in mixing the solution of the double sulphates of magnesia, and the alkalies with freshly precipitated carbonate of baryta, and passing washed carbonic acid through the mixture for a considerable time. The sulphate of baryta which is then produced is filtered off, the solution evaporated to dryness, and the mass heated nearly to redness. A mixture of carbonate of baryta, magnesia, and alkaline carbonate is thus obtained, from which the latter may be extracted with water, converted into chloride, and weighed.

7. CARBONATE OF POTASSA AND MAGNESIA.*

$KO, CO_2; 2(MgO, CO_2) + 9 HO.$

When ignited, this salt loses three-fourths of its carbonic acid, and the whole of its water, leaving a mixture of carbonate of potassa and magnesia, which may be separated by water, and quantitatively determined, the potassa for this purpose being converted into chloride of potassium. The magnesia should not be washed longer than is necessary, since it is not entirely insoluble in water. (Magnesia is more soluble in hot water, and on this account cold is preferable.)

The total quantity of carbonic acid contained in the salt is determined by expelling it in an apparatus arranged for the quantitative determination of carbonic acid. The amount of water may then be inferred by difference.

The joint weight of the water and carbonic acid may be determined by fusing a quantity of vitrified borax in a platinum crucible, weighing when cool, introducing the salt, again weighing, and fusing over the gas flame until all the carbonic acid is evolved, and the fused borax becomes clear. The loss of weight expresses the joint amount of water and carbonic acid.

8. EPSOM-SALT AND GLAUBER'S-SALT.

$MgO, SO_3 + 7 HO$ and $NaO, SO_3 + 10 HO.$

One hundred parts of pure sulphate of magnesia give, by the method described in No. 6, 45.12 parts of phosphate of magnesia. A specimen of Epsom-salt adulterated with Glauber's salt will give a proportionally smaller quantity of the phosphate. Since 45.12 parts of $2\,MgO, PO_5$ correspond to 100 parts of crystallized sulphate of magnesia, a specimen of the latter which yields, for example, only 40 parts of $2\,MgO, PO_5$ would contain only 88.3 per cent. of true Epsom-salt, and 11.7 per cent. of Glauber's-salt.

---

* Obtained in crystals on mixing a solution of chloride of magnesium with a warm saturated solution of bicarbonate of potassa.

In order to test Epsom-salt for Glauber's-salt, the specimen is mixed with powdered charcoal, dried, and heated in a crucible to bright redness. If sulphate of soda be present, water will dissolve out of the cold mass sulphide of sodium, which, when treated with hydrochloric acid, is converted into chloride of sodium, with evolution of sulphuretted hydrogen.

Or the solution of the salt to be tested may be precipitated by hot saturated baryta-water, filtered, the excess of baryta precipitated from the solution by a mixture of ammonia and carbonate of ammonia, and the filtrate evaporated, when, if any Glauber's-salt have been present, carbonate of soda will be left.

9. PHOSPHATE OF SODA AND AMMONIA.*

$$NaO, NH_4O, HO, PO_5 + 8\,HO.$$

A weighed quantity of the salt is gradually and cautiously heated in a platinum crucible, the heat being finally raised to ignition, and continued till the salt is in a state of tranquil fusion. The ammonia and water are thus expelled, their joint amount being indicated by the loss of weight. The fused residue is NaO, PO_5.

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* Six parts of crystallized phosphate of soda are dissolved, with the aid of heat, in 2 parts of water, and in this solution 2 parts of chloride of ammonium are dissolved. The filtered liquid deposits crystals of the new salt which are purified by solution in hot ammoniacal water and recrystallization.

The determination of the ammonia is effected as in No. 5, with another portion of the salt.

In order to determine the phosphoric acid, the salt is dissolved in water and mixed with chloride of ammonium, ammonia and sulphate of magnesia, the precipitatate being treated as in No. 6. The ignited $2MgO, PO_5$ contains 63.55 per cent. of phosphoric acid.

For the direct determination of the soda, a weighed quantity of the salt is dissolved in water, and the phosphoric acid precipitated by acetate of lead. From the filtered liquid, the excess of oxide of lead is removed by a mixture of ammonia and carbonate of ammonia, the solution heated to ebullition, filtered, evaporated to dryness and the residual acetate ignited, with access of air, until the carbonate of soda is colorless.

As a control for the determination of the phosphoric acid, the phosphate of lead may be decomposed by heating with dilute sulphuric acid, and the phosphoric acid precipitated from the filtrate by sulphate of magnesia, as directed above.

10. PHOSPHATE OF MAGNESIA AND AMMONIA.*

$$2\,MgO, NH_4O, PO_5 + 12\,HO.$$

By ignition the salt is converted into $2\,MgO, PO_5$.

The ammonia is determined by dissolving the salt in the smallest possible quantity of hydrochloric acid, mixing the solution with bichloride of platinum and alcohol, and treating the ammonio-chloride of platinum, as in No. 5.

In order to separate and determine the phosphoric acid and magnesia, the ignited salt is fused in a platinum crucible, over a spirit-lamp, with 4 parts of carbonate of potassa and soda.* The mass is digested with water, the residual magnesia washed, ignited and weighed.

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* Prepared by precipitating a solution of sulphate of magnesia to which much chloride of ammonium has been added, by phosphate of soda, and washing the precipitate with dilute ammonia.

The alkaline solution is neutralized with acetic acid, and the phosphoric acid precipitated by acetate of lead. The precipitate is filtered off, washed, dried, detached as far as possible from the filter, which is incinerated in a porcelain crucible, in which the precipitate is then gently ignited and weighed. Since its composition is variable, the quantity of the phosphoric acid cannot be calculated from it. In order to determine this acid, the precipitate is dissolved in warm dilute nitric acid, and the oxide of lead separated by sulphuric acid, alcohol being afterwards added to complete the precipitation.

The sulphate of lead is filtered off, washed, ignited and weighed. From the amount of this precipitate, that of the phosphoric acid may be calculated.

The phosphate of magnesia and ammonia may also be dissolved in acetic acid, the phosphoric acid precipitated by acetate of lead, the excess of oxide of lead removed from the filtrate by adding a mixture of ammonia and carbonate of ammonia, heating and filtering. The solution, which contains acetate of magnesia, is evaporated, and the residue ignited, until the magnesia is perfectly white.

Another method of separating phosphoric acid and magnesia consists in dissolving the ignited salt in a little hydrochloric acid, boiling the solution for some time in order to convert the phosphoric acid into the tribasic form, and mixing it, first, with solution of sesquichloride of iron, and afterwards, with excess of acetate of ammonia; if the solution be now boiled for some time, all the phosphoric acid and iron are precipitated, and the magnesia remains in solution. The filtered liquid is evaporated to dryness, the residue heated till all ammoniacal salt is expelled and moistened with sulphuric acid to convert the magnesia into sulphate. The excess of acid is expelled by heat, and the residual salt gently ignited; from the weight of this residue that of the magnesia, and consquently of the phosphoric acid, is calculated.

---

* Consisting of equivalent proportions of KO, CO_2 and NaO, CO_2, or 13 parts of the former, and 10 of the latter. Also easily obtained by igniting Seignette-salt free from lime, dissolving, and evaporating to dryness.

11. THE CHLORIDES OF POTASSIUM, SODIUM, AND MAGNESIUM.

In the analysis of minerals which are decomposed by hydrochloric acid, there is frequently obtained, after the separation of the other constituents, a mixture of the above-mentioned chlorides. The solution, if containing, as is generally the case, ammoniacal salts, is evaporated to dryness, and the mass gently ignited in a platinum crucible until the latter are volatilized. The magnesia and alkalies are then separated according to one of the following methods:—

I. The mass is moistened with a concentrated solution of carbonate of ammonia, dried and ignited, during which operation, a fragment of carbonate of ammonia is held within the partially closed crucible. This process is repeated until a constant weight is obtained. A mixture of magnesia and alkaline chlorides is left, from which the latter may be extracted by water. This method is more difficult of execution in proportion as more alkaline chlorides are present.

II. The residue containing the three chlorides is mixed in a platinum crucible, with some water and a quantity of finely-powdered oxide of mercury; the mixture is digested for some time, dried, and ignited in a covered crucible, when all the chloride of magnesium is decomposed and converted into magnesia.

III. The chlorides are dissolved in a little water, and the solution boiled for a long time with freshly precipitated carbonate of silver, when all the chloride of magnesium is decomposed. The precipitate is filtered off, washed, and the precipitated carbonate of magnesia dissolved out with dilute hydrochloric acid.

IV. The solution of the bases is mixed with some sal-ammoniac and ammonia in excess, and the magnesia precipitated by phosphate of ammonia (*see* No. 6). From the filtrate the ammonia is expelled by evaporation, and the excess of phosphoric acid precipitated by acetate of lead as a compound of phosphate and chloride of lead. The excess of oxide of lead is precipitated by a mixture of ammonia and carbonate of ammonia; the liquid digested, and the precipitate filtered off. The alkalies are then obtained by evaporation.

V. The chlorides are converted into nitrates by heating with about six times their weight of nitric acid. The solution is evaporated, the salts moistened several times, digested with crystals of oxalic acid whereby all the nitric acid is decomposed.

From the residual mixture of magnesia and alkaline carbonates, the latter are extracted with water.

VI. The magnesia may be precipitated by sesquicarbonate of ammonia and ammonia, and washed with the same. If potash is present in this precipitate it may be dissolved out with water after ignition.

VII. Should the three bases be in form of sulphates, the process indicated in No. 4 must be adopted, or they are weighed after ignition, dissolved in a little water, the solution weighed, about one half poured off, and the remainder weighed. From one portion the magnesia is precipitated by ammonia and phosphate of soda, and from the other potassa by bichloride of platinum.

12. DOLOMITE AND BITTER-SPAR.

$CaO, CO_2; MgO, CO_2$.

The mineral dried at 100° is dissolved in dilute nitric acid, the solution afterwards heated, in order to oxidize any protoxide of iron, neutralized with ammonia, heated to ebullition till it no longer smells of ammonia, and rapidly filtered from any precipitate of sesquioxide of iron. The lime is then precipitated by oxalate of ammonia. When the precipitate has subsided, after being digested for some time, it is filtered off, washed, dried and ignited; it is then moistened with carbonate of ammonia, again dried, and gently heated. It is weighed as carbonate of lime. Or it may be moistened with concentrated sulphuric acid, the excess of acid being expelled by evaporation and subsequent ignition, and weighed as sulphate of lime.

After the filtered liquid has been mixed with excess of ammonia, the magnesia is precipitated by phosphate of soda, and the precipitate treated as in No. 6.

The quantity of carbonic acid contained in the mineral may be determined by loss. It may also be ascertained directly by means of the apparatus arranged for the quantitative determination of carbonic acid.

13. BONE-ASH.

$3CaO,PO_5$ with $3MgO,PO_5$ and CaO,CO_2.

A mass of white burnt bone is dissolved in dilute nitric acid, the solution digested for some time to expel all the carbonic acid, and the phosphates of lime and magnesia precipitated by ammonia. When the precipitate has separated, the solution, which contains the lime previously in combination with carbonic acid, is rapidly filtered, and the precipitate thoroughly washed with ammoniacal water.

From the filtrate, the lime is precipitated by oxalate of ammonia, and the precipitate treated as in No. 12.

The precipitate of phosphates of lime and magnesia is dissolved in the smallest possible quantity of hydrochloric acid, and the lime precipitated by neutral oxalate of potassa. The mixture is digested for some time at a gentle heat, to promote the separation of the precipitate, and the clear supernatant fluid is then cautiously neutralized with carbonate of potassa, in order to precipitate the oxalate of lime dissolved by the liberated oxalic acid; as soon as it has completely separated, the precipitate is filtered off. From the filtrate, which contains all the phosphoric acid and magnesia, the latter is precipitated by ammonia as phosphate of magnesia-ammonia, which is treated as in No. 6.

From the liquid filtered from this precipitate, which must contain free ammonia, the phosphoric acid is precipitated by sulphate of magnesia.

The very small quantity of fluoride of calcium contained in bones can only be detected qualitatively; in the precipitate obtained by saturating the solution of bone-ash in nitric acid with ammonia.

Bone-ash may also be analyzed in the following manner: The finely-powdered substance is heated for a long time, nearly to boiling, with an excess of dilute sulphuric acid, the greater part of the water is then evaporated, and the mass mixed with twice its volume of absolute alcohol, which dissolves the phosphoric acid. The mixture is filtered, and the sulphates washed with alcohol. From these the sulphate of magnesia and a part of the sulphate of lime are extracted with water, and separated as in No. 12. The sulphate of lime remaining undissolved is ignited and weighed. The phosphoric acid solution is mixed with water, the alcohol evaporated, and the phosphoric acid then precipitated by sulphate of magnesia and ammonia as in No. 6.

A third method, based upon the insolubility of phosphate of binoxide of tin in nitric acid, is as follows: The weighed bone-ash is heated in a flask, with moderately strong nitric acid, and several times its weight of pure tin (tin-foil), the weight of which must be accurately known; the contents of the flask are heated to ebullition, diluted with water, and the binoxide of tin, which contains the whole of the phosphoric acid, is filtered off, washed, dried, ignited and weighed. The difference between the weight of this precipitate and that of the binoxide of tin which should be furnished by the amount of metal employed, is due to phosphoric acid. The separation of the lime and magnesia contained in the solution is effected as in No. 12.

A fourth method, applicable in general for the separation of phosphoric acid from bases, consists in dissolving the substance to be analyzed in a small quantity of nitric acid, adding nitrate of silver, some carbonate of silver, and shaking the mixture. All the phosphoric acid combines with the oxide of silver and is precipitated, while the bases remain in solution and may be separated from the excess of silver by hydrochloric acid.

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14. APATITE.

$$3\,(3\,CaO,\,PO_5) + CaCl\ (or + CaF).$$

For the determination of the chlorine, a weighed portion of the mineral (which need not be powdered) is dissolved in dilute nitric acid,* and the chlorine precipitated by nitrate of silver.

In order to detect the small quantity of fluorine which is contained in some specimens of apatite, the finely powdered mineral is mixed, in a platinum crucible, with concentrated sulphuric acid, and the crucible covered with a glass plate coated with a thin film of wax, through which some characters have been written with a needle; the crucible is then heated with a flame so small as not to melt the wax. If fluorine be present, the characters are found etched upon the glass after the removal of the wax. The quantity of the fluorine is inferred from the loss of weight in the whole analysis.

The phosphoric acid and lime may be determined by the methods described in the analysis of bone-ash. The following process may also be employed.

The mineral is dissolved in nitric acid, in a dish, and so much pure mercury added that, after saturating the acid, a portion still remains undissolved. The mixture is then evaporated to perfect dryness on the water-bath. Should it still emit an odor of nitric acid, this acid must be completely expelled by adding more water, and again evaporating to dryness. The mass is treated with water, filtered through the smallest possible filter, and the residue, which contains all the phosphoric acid, well washed.

The solution contains, besides the excess of the mercury-salt, the whole of the lime. The suboxide of mercury is precipitated by hydrochloric acid. Any protoxide of mercury which may have been formed, is precipitated from the filtrate by ammonia. If the mineral contain iron, or other bases precipitable by ammonia, these will remain behind on igniting this precipitate. From the solution, which should be filtered rapidly, and with as little exposure to air as possible, the lime is precipitated by oxalate of ammonia.

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* Many compact apatites, when treated with nitric acid leave a small quantity of crystalline powder, which is cryptolite (phosphate of protoxide of cerium).

The filter with the mercury-residue, which contains the phosphoric acid, is well dried, and the contents thrown into a platinum crucible in which they are mixed with carbonate of potassa and soda; the filter is rolled up and buried in a mixture. The crucible is now heated (but not to redness) under a chimney with a good draught, until the mercury is volatilized, after which the mass may be heated to redness and fused. It is then dissolved in water, an excess of hydrochloric acid added, and the phosphoric acid precipitated by ammonia and sulphate of magnesia.

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15. BARITE, CELESTITE, AND GYPSUM,

$BaO, SO_3.—SrO, SO_3.—CaO, SO_3+2\ HO.$

The water in gypsum is determined by ignition. The salts of strontia and lime are converted into carbonates by action of a solution of carbonate of ammonia at ordinary temperature, while the sulphate of baryta remains unaltered.

At a boiling heat or with carbonate of soda the decomposition is not so complete.

The mixed salts must be finely powdered and well washed with cold water. Nitric acid dissolves the strontia and the lime, but does not act upon the sulphate of baryta.

The latter can be decomposed by fusing with four times its weight of carbonate of potassa and soda.

The mass is then treated with boiling water, the carbonate of baryta filtered off while hot, and washed with boiling water.

The filtered solution is carefully neutralized with hydrochloric acid, the sulphuric acid precipitated by chloride of barium, and the precipitate treated as in No. 3.

The earthy carbonates are dissolved in dilute nitric acid, taking care to obtain a nearly neutral solution, which is then evaporated to perfect dryness in a flask capable of being closed. The saline mass is treated with about twice its volume of a mixture of equal volumes of ether and absolute alcohol, with which it is allowed to digest, in the closed flask, for a long time, being frequently shaken, but not heated. The mixture dissolves the nitrate of lime only. The mixture is filtered, and the undissolved nitrate of strontia washed with absolute alcohol in a closely covered funnel.

The alcoholic solution is diluted with water, the greater part of the alcohol evaporated, and the lime precipitated, as in No. 12, by oxalate of ammonia.

The nitrate of strontia is dried at 100° and weighed, or may be converted into a sulphate with sulphuric acid.

To separate carbonates of baryta and strontia they are dissolved in nitric acid, the solution concentrated and the baryta precipitated by freshly-prepared hydrofluo-silicic acid, previously mixed with an equal volume of alcohol. The silico-fluoride of barium is collected on a weighed filter, washed with weak spirit, and dried.

The filtrate containing the strontia is mixed with sulphuric acid, evaporated to dryness, the sulphate of strontia ignited, and weighed.

If baryta and lime only are to be separated, the solution is largely diluted, the baryta precipitated by sulphuric acid, and the lime separated from the filtrate by oxalate of ammonia, after previously neutralizing with ammonia.

For the separation of baryta and strontia, neutral chromate of potassa may also be employed, which precipitates all the baryta as chromate; the latter is washed, dried, ignited and weighed. It is necessary, however, that the solution should be perfectly neutralized and largely diluted. The strontia may afterwards be precipitated by neutral carbonate of ammonia.

The neutral salts of lime, mixed with a solution of arsenious acid, give with ammonia a precipitate of arsenite of lime. The salts of strontia and baryta treated in the same way do not form a precipitate. On the other hand, the presence of strontia in a salt of lime may be shown by a clear solution of sulphate of lime.

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16. ALUMINA-ALUM.

$$KO, SO_3; Al_2O_3, 3\ SO_3 + 24\ HO.$$

A weighed quantity of the pure salt is dissolved in water, and the sulphuric acid precipitated by chloride of barium (*see* No. 3).

From the solution filtered from the sulphate of baryta, the alumina is precipitated, together with the excess of baryta which has been added, by a mixture of carbonate of ammonia and free ammonia. After gently heating for some time, the precipitate is filtered off, the solution evaporated, and the saline mass heated till all the chloride of ammonium is volatilized. The gently-ignited residue is chloride of potassium.

The precipitate containing alumina and baryta is dissolved in dilute hydrochloric acid, and the baryta precipitated by sulphuric acid.

From the solution filtered from the sulphate of baryta, the alumina is precipitated by carbonate of ammonia, or better, by sulphide of ammonium, either of which effects a more complete precipitation than caustic ammonia.

The precipitated hydrate of alumina is well washed, for which purpose hot water is to be preferred, and strongly ignited in order to expel the water.

The water contained in the alum is determined by loss. It may also be estimated directly by carefully exposing the salt for a very long time to a gradually increasing heat, which must finally be raised to dull redness.

17. IRON-AMMONIA-ALUM.[*]

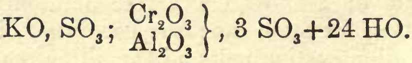
$$NH_4O,\ SO_3;\ Fe_2O_3,\ 3\ SO_3+24\ HO.$$

At a strong red heat, this salt is entirely decomposed, leaving pure sesquioxide of iron.

The determination of ammonia is effected as in No. 5; that of sulphuric acid according to No. 3.

In order to control the determination of the sesquioxide of iron, another portion of the salt is dissolved in water, and the sesquioxide precipitated by ammonia. The precipitated hydrate is washed, dried, and ignited.

18. ALUMINA-CHROME-ALUM.[†]



$$KO,\ SO_3;\ \left.\begin{matrix}Cr_2O_3\\ Al_2O_3\end{matrix}\right\},\ 3\ SO_3+24\ HO.$$

The sulphuric acid is precipitated by chloride of barium as in No. 3.

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[*] Powdered red or brown iron-stone is digested with concentrated sulphuric acid; the white sulphate thus produced is dissolved in water, the solution mixed with sulphate of ammonia, filtered and allowed to crystallize.

[†] Three parts of finely-powdered bichromate of potassa are mixed with 15 parts of water, and 1 part of concentrated sulphuric acid is gradually âdded, so that no evolution of heat may ensue; sulphurous acid gas is then passed through the solution, which is

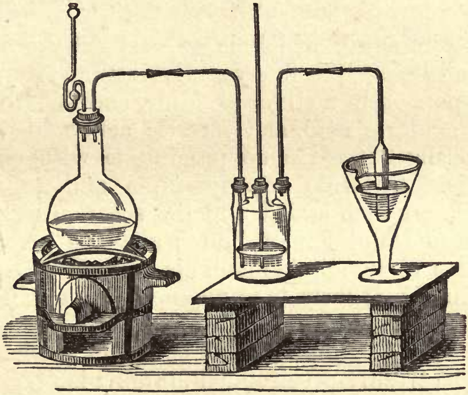
The alumina, sesquioxide of chromium, and excess of baryta are precipitated from the filtrate by carbonate of ammonia mixed with caustic ammonia. After long standing, the precipitate is filtered off and thoroughly washed.

The filtrate is evaporated, the residue heated to expel chloride of ammonium, and the residual chloride of potassium gently ignited in a covered crucible.

The mixed precipitate is taken and washed off while wet from the filter, dissolved in dilute sulphuric acid, and the sulphate of baryta, filtered and washed.

An excess of caustic potassa is added to the solution, which is then saturated with chlorine gas, and the oxide of chromium forms a yellow solution of chromate of potassa.

Fig. 2.



kept cool, so that its temperature may not rise above 40°, until the odor of the gas begins to be perceptible. After some time, octohedra of pure chrome-alum are formed, which may be set aside. The mother-liquor is mixed with an equal volume of a solution of common alum, saturated at 40°, when the salt in question separates in yellowish octohedra.

Only a small quantity of alumina is dissolved which may be precipitated by gentle digestion with carbonate of ammonia.

The solution of alkaline chromate filtered from the alumina is carefully mixed with excess of hydrochloric acid and some alcohol, and heated until it has a pure emerald-green color. The sesquioxide of chromium is precipitated from the hot solution by caustic ammonia, washed, dried, ignited, and weighed.

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19. WAVELLITE AND PHOSPHATES OF ALUMINA IN GENERAL.

$$Al_2 O_3, PO_5 + 12 HO.$$

I. The mineral, which is only slightly soluble in hydrochloric acid, is finely pulverized and fused with caustic potassa in a silver crucible, and then dissolved in hydrochloric acid, and tartaric acid added to the solution until it gives no precipitate with excess of ammonia. Chloride of ammonium and sulphate of magnesia are then added, and the solution well closed allowed to stand for 24 hours, and the precipitated phosphate of magnesia-ammonia treated as in No. 6. It contains basic tartrate of magnesia, which after ignition is re-dissolved in hydrochloric acid, heated for a long time, and again precipitated by ammonia.

II. The freshly-precipitated alumina is dissolved in the smallest possible quantity of caustic soda, the solution diluted, heated to ebullition, and a solution of silicate of soda added as long as any precipitate of silicate of alumina is produced. Lastly, in order to precipitate the whole of the silicic acid, a concentrated solution of sal ammoniac is added, the solution again boiled and filtered. From the filtrate, the phosphoric acid is precipitated by ammonia and sulphate of magnesia.

The silicate of alumina is decomposed by concentrated hydrochloric acid, the mass evaporated to dryness on the water-bath, the residue moistened with hydrochloric acid, the alumina-salt extracted with water, and the alumina precipitated by carbonate of ammonia.

III. The weighed alumina containing phosphoric acid is dissolved in concentrated nitric acid, and the solution heated with about the same quantity (accurately weighed) of pure tin (tin-foil). The mixture is diluted with water, heated until boiling, and the binoxide of tin which has combined with the whole of the phosphoric acid is filtered off, washed, and ignited. The difference between the weight of this precipitate and that of the binoxide of tin which should have been furnished by the metal employed represents the phosphoric acid. The alumina is then precipitated from the solution by sulphide of ammonium.

Or chloride of tin is added to the solution of phosphate of alumina, heated to boiling, and the oxide of tin and all the phosphoric acid precipitated by sulphate of soda. If sesquioxide of iron is present, a portion of it is thrown down. The accuracy of this method is not yet determined.

20. SPINEL. (ALUMINA AND MAGNESIA IN GENERAL.)

$MgO, Al_2O_3.$

The mineral is very finely pulverized in a steel mortar separated from the iron with hydrochloric acid, and then fused with at least six times its weight of bisulphate of potassa.* It should be kept in a state of fusion for a long time, without the disengagement of too much sulphuric acid. The mass is then dissolved in water containing a little hydrochloric acid, chloride of ammonium added, and the alumina precipitated by ammonia. In order to free it from any magnesia, the fluid is heated to boiling until no more ammonia is given off.† The gelatinous alumina is filtered, and allowed to partially dry upon the funnel when it may be completely washed. It is ignited and weighed. The magnesia is precipitated by phosphate of soda and ammonia. Many specimens of spinel contain a little protoxide of iron and silica.

The red spinel contains sesquioxide of chromium, which may be separated from the alumina as in No. 18.

21. ALUMINA AND SESQUIOXIDE OF IRON.

The mixture of the two is dissolved in hydrochloric acid, the greater part of the excess of acid evaporated, the solution mixed with an excess of pure solution of potassa and heated nearly to the boiling point. The alumina is thus dissolved, the sesquioxide of iron being left behind of a dark brown color. The solution is filtered off, acidulated with hydrochloric acid, and the alumina precipitated by sulphide of ammonium.

The sesquioxide of iron, which contains some potassa, is dissolved in hydrochloric acid, re-precipitated by ammonia, and ignited.

This method of separation is unsafe, and unless repeated more than once, incomplete. It is better to heat the acid solution to ebullition, to add sulphite of soda, in order to reduce the sesquioxide of iron to the state of proto-sesquioxide, replace the solution over the lamp, boil for some time and then neutralize with carbonate of soda, and afterwards boil with excess of caustic soda until the precipitate is black and pulverulent.

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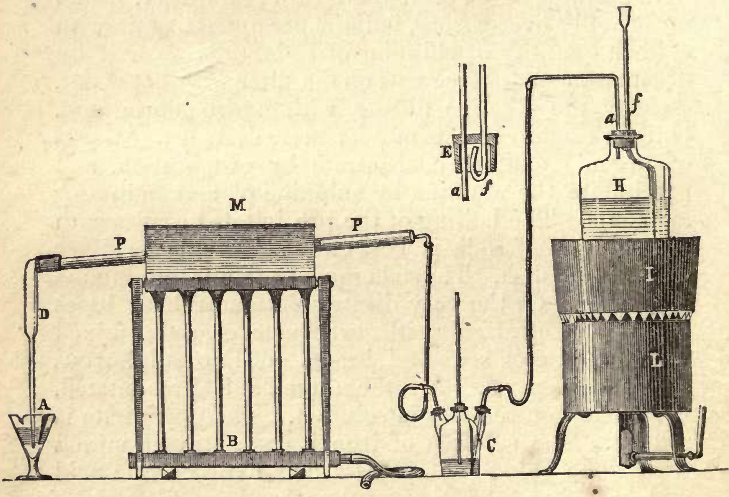
* Prepared by heating equal parts of neutral sulphate and concentrated sulphuric acid to a dull red heat until the the mixture flows quietly.

† The same process as in the separation of alumina and lime.

The tendency to bumping preceding the actual ebullition of the fluid, may be guarded against by means of a spiral coil of platinum wire placed in the liquid, or by constant agitation of the latter; when ebullition has once set in, there is no further need of these precautions. Remove the liquid now from the gas, allow to deposit, pass the clear fluid through a filter, which must not be over-porous, boil the precipitate again with a fresh quantity of solution of soda, then wash it by decantation and afterwards on the filter with hot water. Acidify the alkaline filtrate with hydrochloric acid, boil with some chlorate of potassa (to destroy any traces of organic matter), concentrate by evaporation, and precipitate the alumina by sulphide of ammonium or ammonia. The boiling of the precipitated oxides with the solution of soda is best effected in a large silver or platinum dish. The soda must be free from alumina and silica. Or the very dilute solution of both bases may be neutralized with carbonate of soda, mixed with sulphite of soda and heated until no sulphurous acid is given off. All the alumina is precipitated, while the iron remains in solution. The precipitate is ignited. The solution of iron is concentrated, mixed with some chlorate of potassa and hydrochloric acid and heated. After the sulphur has been filtered off the iron is precipitated by ammonia.

The separation may be obtained by placing the mixed precipitate, ignited in a porcelain boat, which is placed in a tube of the same material heated to redness, through which a current of dry hydrogen is passed, and which it is necessary to maintain until it is completely cool. Then there should be substituted in place of the current of hydrogen, a current of hydrochloric acid gas, which transforms the iron into volatile chloride and leaves the alumina, which is weighed. A complete description of this process of separation of iron and alumina may be found in the article on silicates. The apparatus is arranged as follows: L is a gas furnace upon which is placed a salt bath I. In the bottle H there is placed some fresh chloride of sodium, on which is poured concentrated hydrochloric acid.

Fig. 3.



Then the bottle H is placed in cold water and sulphuric acid gradually poured upon it, taking care that the mixture does not become heated, and stopping when vapors of hydrochloric acid begin to form. It is sufficient to heat this mixture to 50° or 60° to evolve a steady current of hydrochloric acid gas.

The amount of sesquioxide of iron may be inferred from the loss of weight, and the result controlled by collecting the chloride of iron which passes over and weighing it.

22. PHOSPHORIC ACID AND SESQUIOXIDE OF IRON.*

In order to separate phosphoric acid from sesquioxide of iron, the compound is ignited with at least an equal weight of carbonate of potassa and soda (No. 10), the resulting mass exhausted with water, the solution supersaturated with hydrochloric acid and then with ammonia, and the phosphoric acid precipitated by sulphate of magnesia.

The residual sesquioxide of iron retains some alkali.

Or the sesquioxide of iron containing phosphoric acid is dissolved in hydrochloric acid, precipitated by ammonia, and digested with excess of sulphide of ammonium (without previous filtration), until all the sesquioxide is converted into sulphide of iron. When the liquid is no longer green, but of a pure yellow color, it is filtered off, and the phosphoric acid immediately precipitated by sulphate of magnesia.

For the accurate quantitative separation of a small quantity of phosphoric acid from a large quantity of sesquioxide of iron, the latter is dissolved in hydrochloric acid, and the solution heated to ebullition with sulphite of soda till its color has changed to a bright green, when all the sesquioxide of iron is converted into protoxide. The solution is boiled till it no longer smells of sulphurous acid, neutralized with carbonate of soda, and, in order to produce a little sesquioxide of iron, mixed with a very little chlorine-water, the quantity of which must be regulated according to the amount of phosphoric acid which is present. The solution must now be mixed with an excess of acetate of soda, when phosphate of sesquioxide of iron separates as a white precipitate. Chlorine-water is then added, drop by drop, until the liquid has assumed a reddish color, when it is boiled, so that the precipitate may collect, and be filtered. From this precipitate the phosphoric acid is separated by sulphide of ammonium, as directed above.

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* For analyses for practice, the phosphate of sesquioxide of iron is prepared by precipitating sesquichloride of iron with phosphate of soda. Or a mixture of phosphates may be prepared by precipitating a solution containing sesquichloride of iron, chloride of calcium, chloride of magnesium, and chloride of manganese.

Or it may be dissolved in hydrochloric acid, boiled with sulphite of soda, and afterwards with excess of caustic soda, till the precipitate is converted into black proto-sesquioxide of iron, which is filtered off. The solution is acidified, and the phosphoric acid precipitated as above.

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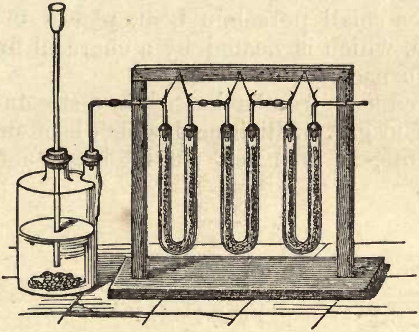
23. HEMATITE, Fe_2O_3, AND LIMONITE, Fe_2O_3, 3 HO.

For the determination of the water, weighed fragments of the ore are heated to redness, for a long time, in a platinum crucible. If the mineral decrepitates, it must first be finely powdered.

In order to determine the oxygen, the fragments of ignited limonite or of hematite are heated to redness in a weighed bulb-tube of very infusible glass (the bulb being as small as possible), through which a stream of dry hydrogen, free from arsenic, is transmitted as long as any water is formed.

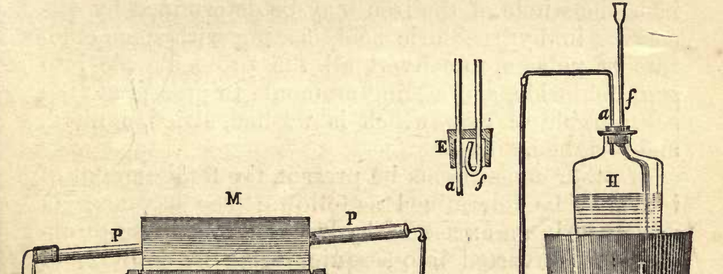
In order to purify hydrogen it is passed through the U tubes containing pumice or fragments of porcelain dipped in a solution of acetate of lead, sulphate of silver, and caustic potassa; the first absorbs the sulphuric

Fig. 4.



acid, the second absorbs the combinations of hydrogen with phosphorus and arsenic, and the last the carburet-

Fig. 5.



ted hydrogen. The reduction must be effected at the highest temperature of the gas-lamp, for otherwise the reduced iron, even when cool, may reoxidize and sometimes inflame in the air. It is safer to reduce the oxide in a small porcelain boat, placed in a tube of porcelain, which is heated by a charcoal fire, or over the gas furnace.

The reduced iron is heated in a stream of hydrochloric acid gas. Silicic acid, which is often contained in limonite, is then left undissolved, and may be weighed.

24. MAGNETITE.*

FeO, Fe_2O_3.

To determine the amount of oxygen which is combined with the iron, the proto-sesquioxide is reduced by hydrogen, as in No. 23.

If the substance contain only proto-sesquioxide of iron, the whole of the iron may be determined by dissolving in hydrochloric acid, heating with some chlorate of potassa, to convert all the protochloride into sesquichloride, and adding ammonia to precipitate the sesquioxide of iron, which is washed, dried, ignited, and weighed.

If other constituents be present, the total amount of iron may be determined as follows: The substance is dissolved in an excess of hydrochloric acid, the protochloride converted into sesquichloride by addition of chlorate of potassa, and all free chlorine expelled by boiling. The solution is then diluted with water until the flask is more than half-full; a weighed strip of bright sheet-copper is placed in the solution, the flask closed by a cork furnished with a narrow glass tube, and the liquid heated to ebullition. It is retained at this temperature until the dark-brown color originally observed has changed to a pale yellowish-green. The whole of the iron is now contained in the solution as protochloride, in consequence of the formation of subchloride of copper. The orifice of the little tube is closed air-tight, and the solution allowed to cool somewhat. The flask is then filled with hot water, the liquid poured off from the undissolved copper, which is to be washed, first with dilute hydrochloric acid, then repeatedly with water, dried, and weighed. The atomic weight of copper is to that of iron as the quantity of copper dissolved is to that of the iron sought.

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* Forge-scales have a similar composition.

In order to determine directly the amount of protoxide and sesquioxide of iron present in a substance, it must be dissolved in hydrochloric acid. The following is the method adopted: The compound is dissolved in an excess of concentrated hydrochloric acid, in a flask filled with carbonic acid, and afterwards closed; the flask is then nearly filled up with water, previously boiled, and a weighed strip of copper introduced; the closed flask is placed in water, which must be gradually heated to boiling, the subsequent process being conducted and the result calculated as directed above.

Or the weighed substance is placed in a flask closed with a cork, and furnished with tubes for ingress and egress, and with a funnel-tube passing to the bottom of the flask, which is to be filled with carbonic acid. Hydrochloric acid is then added through the funnel-tube, and the solution assisted by heat, whilst carbonic acid is allowed to stream through the apparatus. The solution is afterwards diluted, through the funnel-tube, with boiled water, and a milky mixture of carbonate of baryta with water gradually added; this precipitates the whole of the sesquioxide of iron, while the protoxide remains in solution. When the supernatant liquid has become clear, it is decanted through the egress-tube, the precipitate again mixed with water, and after the clear liquid has been again decanted, quickly thrown upon a filter, and rapidly washed, air being excluded, with water which has been previously boiled and allowed to cool.

The iron precipitate is dissolved in dilute hydrochloric acid, the baryta separated by sulphuric acid, and the sesquioxide of iron precipitated by ammonia.

The solution, which contains the protoxide of iron, is mixed with hydrochloric acid and chlorate of potassa, and concentrated by evaporation; the baryta is then precipitated by sulphuric acid, and afterwards the sesquioxide of iron by ammonia.

25. SIDERITE.

FeO, CO_2, frequently containing MnO, CO_2,—CaO, CO_2, and MgO, CO_2.

I. The best method of analysis, which is especially applicable where but little manganese is present, is the following: A weighed portion of the powdered ore, previously dried, is dissolved in hydrochloric acid, with the aid of heat, nitrate or chlorate of potassa being added from time to time, so that the whole of the protoxide of iron is sure to be converted into sesquichloride. The solution, which must still be acid, so that chloride of ammonium may be formed, is diluted, and gradually neutralized with dilute ammonia, until it has acquired a dark brown-red color, and a small quantity of hydrated sesquioxide of iron is precipitated. The whole of the sesquioxide of iron is then separated by neutral succinate of ammonia, while protoxide of manganese, lime, and magnesia remain in solution. The precipitated succinate of sesquioxide of iron is rapidly filtered off, washed with cold water, dried, and gradually heated to redness in a porcelain crucible, with free access of air, till it is converted into pure sesquioxide of iron.

The filtrate is feebly acidulated with hydrochloric acid, evaporated to dryness, and heated till all ammoniacal salts are expelled.

The residue is then dissolved in a small quantity of water, with addition of hydrochloric acid, the solution saturated with chlorine, and the manganese precipitated as hydrated sesquioxide by addition of ammonia. The liquid is rapidly filtered off, so that no carbonate of lime may be precipitated, and the manganese-precipitate washed, dried, and ignited, when it is converted into brown proto-sesquioxide.

The lime and magnesia in the filtrate are separated as in No. 12.

Or the manganese may be precipitated by sulphide of ammonium, the sulphide of manganese rapidly filtered off, and dissolved in hydrochloric acid. When all the sulphuretted hydrogen has been expelled by evaporation, the solution is heated with carbonate of soda, when the manganese is precipitated as carbonate, which, after ignition, leaves the brown proto-sesquioxide.

From the solution filtered from the sulphide of manganese, the lime and magnesia are precipitated as in No. 12.

II. The acid solution is largely diluted with water, and carbonate of soda gradually added (drop by drop, when the solution is neutral), with constant stirring, until all the sesquioxide of iron is precipitated. The other bases remain dissolved in the free carbonic acid. The manganese is then best precipitated by hypochlorite of soda, in the cold.

III. When a larger quantity of manganese is present, the solution, which must contain the iron entirely in the form of sesquichloride, and must not be too acid, is gradually mixed with carbonate of baryta, which precipitates the sesquioxide of iron only. When a slight excess of carbonate of baryta has been added, and the solution well stirred, it is filtered. The washed precipitate is dissolved in dilute hydrochloric acid, the baryta precipitated by sulphuric acid, and the sesquioxide of iron by ammonia.

From the solution which contains the other three bases, the dissolved baryta is first precipitated by sulphuric acid, and the solution treated as in No. 12.

IV. The diluted solution, obtained as in I, is neutralized with carbonate of soda till it has a dark brown-red color, mixed with a saturated solution of acetate of soda, and chlorine gas passed into it which precipitates the manganese, or it is heated to ebullition, when the whole of the sesquioxide of iron is precipitated.

The filtrate is neutralized with carbonate of soda, mixed with hypochlorite of soda (containing bicarbonate of soda), and allowed to stand in a closed vessel for twenty-four hours, when the manganese is precipitated as hydrated sesquioxide, which is ignited and weighed as proto-sesquioxide.

From the filtered liquid the lime and magnesia are separated as above.

V. The solution of oxide of iron is precipitated by ammonia, the liquid boiled as long as ammonia is given off, and the oxide of iron filtered off, which is now free from lime, magnesia, and manganese, It may be filtered with free access of air, for the fluid contains no free ammonia. The solution is concentrated by evaporation and the three bases precipitated by an excess of carbonate of potassa, and boiled until ammonia ceases to be disengaged.

It is then filtered, the precipitate dissolved in nitric acid, evaporated to dryness, and the saline mass carefully raised to a dull red heat. The lime and magnesia may be separated by very dilute nitric acid from the oxide of manganese, which is insoluble in the acid.

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26. BOG IRON-ORE.

Fe_2O_3, 3 HO, with MnO, Al_2O_3, CaO, MgO, SiO_3, PO_5, AsO_5.

If the amount of iron only is to be determined, the process with copper may be employed, as in the case of magnetic iron; or the ore may be subjected to the dry assay. The complete analysis is effected in the following manner:—

The mineral, dried at 100°, is ignited, and the water determined.

Another portion, which has not been ignited, is coarsely powdered, and dissolved in hydrochloric acid; the solution is evaporated to perfect dryness on the water-bath, the mass dissolved in warm dilute hydrochloric acid, and the sand and silicic acid removed by filtration. The latter may, after ignition and weighing, be separated from the sand by boiling with carbonate of soda.

The hydrochloric solution is boiled with an alkaline sulphite, until it no longer smells of sulphurous acid, to reduce the sesquichloride of iron to protochloride, and the arsenic acid to arsenious acid, which is then precipitated by sulphuretted hydrogen, as tersulphide of arsenic; sometimes mixed with a little sulphide of copper.

The solution is boiled till the sulphuretted hydrogen is completely expelled, precipitated by carbonate of soda, mixed with an excess of caustic soda, and boiled until the precipitate becomes pulverulent.

The solution is filtered off. It contains all the alumina and part of the phosphoric acid, which are separated as in No. 19.

The precipitate, consisting of proto-sesquioxide of iron, carbonate of protoxide of manganese, carbonate and phosphate of lime and magnesia, is dissolved in hot nitric acid; the solution is neutralized, as far as possible, with carbonate of soda, mixed with acetate of soda, and boiled, when all the phosphoric acid and sesquioxide of iron are precipitated. In order to separate these, the precipitate is treated as in No. 22.

The filtrate contains the protoxide of manganese, lime, and magnesia, which are separated as in No. 25.

27. WET ASSAY OF IRON.

(Volumetric Method.)

The process for determining in the moist way with great accuracy, and without a complete analysis, the amount of iron contained in an ore, consists in ascertaining the number of measures of a solution of permanganate of potassa of known strength which may be decolorized by the solution of protoxide of iron obtained from a given quantity of the ore.*

One equiv.=1·980 grms. of crystallized permanganate of potassa converts the protoxide of iron from 10 equivs.=3·500 grms. of pure iron into sesquioxide.

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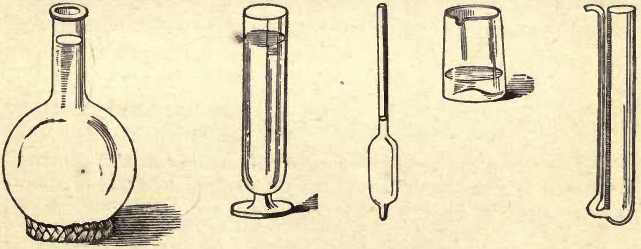
* To prepare the permanganate of potassa, 10 parts of very finely powdered pyrolusite are mixed with 7 parts of chlorate of potassa, the mixture saturated with a very concentrated solution of 10 parts of hydrate of potassa and the wet mass gradually heated in an earthen crucible to dull redness, so that it cinders together, but does not fuse. When cool, it is powdered, treated, in a flask, with a considerable quantity of hot water, and washed carbonic acid gas passed into it until the color of the solution has changed to a purple-red, and the excess of potassa is converted into the carbonate. It is then allowed to stand until the solution becomes clear, which is poured off from the precipitate and evaporated to the point of crystallization. The salt is then purified by recrystallization.

So that if 19·80 grms. of the salt be dissolved in 1 litre (=1000 grms. or 1000 cub. cent.) of water; 100 cub. cent. of this solution will correspond to 3·50 grms. of iron. It must be kept in a well-stoppered bottle.

An equivalent quantity (say 3·5 grms., or half that amount) of the ore to be tested is dissolved in concentrated hydrochloric acid, in a capacious flask, by the aid of heat. If the insoluble residue of foreign matters, such as clay, silica, &c., be not very considerable, it is unnecessary to filter the solution. The iron must now be entirely reduced to the state of protoxide, either by mixing the solution with several times its volume of a saturated solution of sulphurous acid, and boiling so long as any trace of that gas is perceptible; or, better, by allowing a piece of zinc, free from iron, to remain in the liquid until its color is changed to a pale green. It is then decanted from the zinc, the latter thoroughly rinsed, the solution diluted with the washing-water, and mixed with some more hydrochloric acid; the solution of permanganate of potassa is then dropped in from a burette (*see* Alkalimetry), until the

Fig. 6. Fig. 7. Fig. 8. Fig. 9. Fig. 10.



The figures 6, 7, 8, 9, 10 represent the burette, the pipette, and the graduated vessels used in volumetric analysis.

yellow color which the solution then acquires is changed to a clear red by adding another drop of the permanganate. The number of cubic centimetres of the manganese-solution which have been employed, at once indicates the percentage of iron in the ore.

Instead of the crystallized permanganate of potassa, the crude solution originally obtained in the preparation of that salt may be employed, provided it be first graduated—that is, quantitatively tested as to its oxidizing power. For this purpose, 3·5 grms. (or half that quantity, 1·75 grms.) of pure iron-wire are dissolved in a capacious flask by concentrated hydrochloric acid, with the aid of heat. The solution is diluted with several times its volume of cold water, and the solution of permanganate dropped into it, as directed above. When the quantity of solution employed has been read off, the whole is diluted with so much water, that 100 cub. cents. may correspond to 3·5 grms. of iron. It must be kept in a well-stoppered bottle.

28. IRON ASSAY.

The weighed iron-ore, in the state of fine powder, roasted or not, as the case may be, is mixed with dried borax, and the mixture exposed for an hour, in a covered crucible lined with charcoal, to the most intense heat of a wind-furnace with a good draught; the quantity of borax varies according to the nature of the iron-ore. The greater the quantity of extraneous matter which is present, the more borax it requires. For 10 grms. of iron-ore, 3 grms. of borax may be taken as the minimum, 10 grms. as the maximum. In a well conducted assay, all the iron is found reduced to a single well-fused button. If the iron ore contained phosphoric acid the crude iron will contain *phosphorus*.

29. SULPHATE OF COPPER.

(Blue Vitriol.)

$CuO, SO_3 + 5\,HO.$

For analysis, the salt is purified by recrystallization.

To determine the water, a weighed quantity of the dry salt, in the state of fine powder, is heated to about 200°, until it has become perfectly white, and has ceased to lose weight.

It is then dissolved in water, and the sulphuric acid precipitated by chloride of barium, as directed in No. 3.

For the determination of copper, another weighed portion of the salt is dissolved in from 50 to 100 times its weight of water, in a dish or a wide-mouthed flask; the solution is heated until boiling, and the oxide of copper precipitated by caustic potassa, which should not be added in too large excess. The brownish-black precipitate is filtered off, washed with hot water, dried, and weighed.

To determine the amount of oxygen in the oxide of copper, a freshly-ignited portion is introduced into a weighed bulb-tube, and its weight carefully ascertained; a stream of dry hydrogen, free from arsenic, is then passed through the tube, the bulb of which is heated to redness with a large flame. When no more aqueous vapor is perceptible, and the oxide is completely reduced to the metallic state, it is allowed to cool in the stream of gas, and weighed as soon as the hydrogen in the tube has been replaced by atmospheric air.

30. CHALCOPYRITE.

$Cu_2S, Fe_2S_3.$

The powdered mineral is introduced into a flask, placed obliquely, and gradually mixed with concentrated nitric acid in small portions at a time; the contents of the flask are then heated until either the whole is dissolved, or the metals have passed into solution together with a portion of the sulphur, and the unoxidized sulphur has separated in the form of a yellow powder, or in fused drops of a clear yellow color. The solution is diluted with water, and decanted from any undissolved sulphur, which is well washed, dried in a porcelain crucible, at a gentle heat, and weighed. It is then burnt in order to ascertain whether it contains any metals or quartz, &c. Should the sulphur be separated in a pulverulent state, it must be collected on a weighed filter, washed, and dried at a very gentle heat.

From the filtered solution, that portion of the sulphur which has been converted into sulphuric acid is precipitated by chloride of barium, and the sulphate of baryta treated as in No. 3. Protracted washing with hot water is necessary, since the precipitate has carried down some nitrate of baryta.

In order to avoid this, the mineral may be dissolved in concentrated hydrochloric acid, with gradual addition of nitric acid, or chlorate of potassa.

The excess of baryta having been removed from the liquid filtered from the sulphate of baryta by means of sulphuric acid, a slow stream of sulphuretted hydrogen is passed through the filtrate, until the odor of the gas is distinctly perceptible. The precipitated sulphide of copper is thrown, as rapidly as possible, upon a dried and weighed filter, and well washed with water containing sulphuretted hydrogen.

It is then dried in the funnel at 200°, weighed, a portion of it introduced into a weighed bulb-tube, which is afterwards again weighed, and heated in a stream of hydrogen until it no longer loses any sulphur. It is thus converted into Cu_2S, which contains the same amount of copper as the protoxide. The weight obtained is calculated upon the whole quantity of sulphide of copper.

Or the filter with its contents may be allowed to dry in the funnel, the precipitate detached, and thrown into a beaker; the filter is then completely incinerated, the ash added to the sulphide of copper, and the latter oxidized with *aqua-regia* till the sulphur separates of a pure yellow color. From the filtered solution, the protoxide of copper, as in No. 29, is precipitated at a boiling heat by caustic potassa, ignited and weighed.

The solution filtered from the sulphide of copper, containing the iron in the form of protoxide, is heated nearly to boiling, in a flask, concentrated if necessary by evaporation, and treated at the same time with chlorate of potassa in small portions, until all the protoxide of iron is converted into sexquioxide, which is then precipitated by ammonia, washed, dried, and ignited.

Notwithstanding the solubility of oxide of copper in caustic ammonia, this reagent will not effect its complete separation from sesquioxide of iron, since the latter carries down with it a considerable quantity of oxide of copper which cannot be extracted by ammonia.

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31. SPHALERITE, OR BLENDE.

ZnS.

The solution is effected just as in the case of chalcopyrite. The mineral must be very finely powdered, and very concentrated acid must be employed.

After the sulphuric acid which is produced has been precipitated by chloride of barium, and the excess of baryta has been removed, the solution is saturated with sulphuretted hydrogen, in order to precipitate any copper and cadmium which often occur in small quantities in this mineral. The precipitatate, after being filtered off and washed, is treated as in No. 36.

The first filtrate, which contains the zinc and generally a little iron, is heated to ebullition, and mixed, first with some hypochlorite of soda to peroxidize the iron, then with excess of ammonia, until all the oxide of zinc is redissolved, and the sesquioxide of iron precipitated; the latter is then washed and ignited. It cannot be obtained by this method perfectly free from oxide of zinc.

From the filtrate, the zinc is precipitated by sulphide of ammonium. The precipitate should not be filtered off until it has separated from the liquid; it is washed with water containing a little sulphide of ammonium, and digested (together with the filter), while yet moist, with concentrated hydrochloric acid, the solution filtered off, and the oxide of zinc precipitated, at the boiling-point, by carbonate of soda. The precipitate is washed, dried, ignited, and weighed as pure oxide of zinc.

Or it may be dried as sulphide of zinc, removed from the filter as much as possible, which is burned, and the ashes added to the sulphide, mixed with a little sulphur, placed in a weighed bulb tube, and ignited in a current of hydrogen, and then weighed as sulphide of zinc.

Sesquioxide of iron may be more completely separated from oxide of zinc by means of succinate of ammonia, as described in No. 25, or by carbonate of baryta (No. 25, III.)

If, as has been proposed, the solution were mixed with acetate of soda, so as to convert the iron and zinc into acetates, and treated with sulphuretted hydrogen, not only zinc, but iron also would be precipitated.

32. SMITHSONITE.

ZnO, CO_2.

This mineral generally contains small quantities of protoxides of iron, manganese, lead, and cadmium, together with lime, magnesia, and silicic acid.

It is dissolved in hydrochloric acid, the solution evaporated to dryness, the mass digested with concentrated hydrochloric acid, diluted, heated, and the silicic acid filtered off.

The solution, which must be acid, is saturated with sulphuretted hydrogen, which precipitates the lead and cadmium.

This precipitate is oxidized with concentrated nitric acid, a little sulphuric acid being also added, evaporated to dryness, and the sulphate of cadmium separated from the sulphate of lead by water. (*See* Lead and Bismuth.)

The filtrate is boiled, to expel the sulphuretted hydrogen, and treated with chlorate of potassa to peroxidize the iron. From the solution, which must still contain free chlorine, the sesquioxides of iron and manganese are precipitated by excess of caustic ammonia, and separated as in No. 25.

The zinc is precipitated from the filtered solution, as sulphide, by addition of sulphide of ammonium, and the precipitate treated as in No. 31. The solution is rapidly filtered off, with as little exposure to air as possible, and the lime precipitated by oxalate of ammonia; the magnesia is afterwards separated by phosphate of soda.

If a specimen of this mineral consist of carbonate and silicate of zinc, their relative quantities may be approximately determined by igniting the finely-powdered mineral, and digesting it with a mixture of carbonate of ammonia and free ammonia, which dissolves the oxide of zinc previously in combination with carbonic acid, leaving the silicate untouched.

33. BRASS.

The alloy is dissolved in hydrochloric acid with gradual addition of nitric acid, the solution diluted, and the copper precipitated by sulphuretted hydrogen. (*See* No. 30.)

The excess of sulphuretted hydrogen is expelled from the filtrate by boiling, and the oxide of zinc precipitated from the hot solution by carbonate of soda. (*See* No. 31.)

Oxide of zinc cannot be entirely separated from oxide of copper by even a very large excess of caustic potassa.

Too little zinc is usually obtained by the above process, because a portion is carried down with the sulphide of copper. The separation is more completely effected by neutralizing the diluted solution of the alloy with ammonia, and digesting with a slight excess of solid hydrate of potassa until it has lost its color and ammoniacal odor. The oxide of copper is then filtered off, and washed with hot water. From the alkaline solution, the zinc is precipitated by sulphide of ammonium, or boiling with carbonate of soda.

Another accurate method is the following: The solution of both metals is saturated with sulphurous acid and the copper precipitated as white subsulphocyanide by sulphocyanide of potassium. After it has digested for some time, the subsulphocyanide is filtered, a little sulphur added and ignited in hydrogen gas,* when it is converted into Cu_2S. The oxide of zinc is heated and precipitated with carbonate of soda.

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* The precipitate with filter ash should be placed in a porcelain crucible, and strongly ignited by a stream of hydrogen, by means of the gas blowpipe.

This method may be used also for the separation of iron and copper.

The brass sometimes contains traces of tin. It is then dissolved in hot nitric acid, which leaves the binoxide of tin (containing a little copper) untouched.

In order to detect a small quantity of lead which frequently occurs in brass, the sulphide of copper precipitated by sulphuretted hydrogen is oxidized with fuming nitric acid, the mass dried, and treated with water, which leaves the sulphate of lead undissolved. Should this contain sulphur, it must be burnt off.

Or the brass may be dissolved in nitric acid, a little sulphuric acid added, the solution evaporated to dryness, and the mass treated with water.

If the brass be placed in a little porcelain boat, and heated to redness in a porcelain tube through which a rapid stream of hydrogen is passed, all the zinc may be volatilized.

34. OXIDES OF MANGANESE, IRON, AND ZINC.

The solution, which must contain the iron in the form of sesquioxide, is mixed with carbonate of soda until a permanent precipitate begins to appear; it is then boiled with acetate of soda, when all the sesquioxide of iron is precipitated.

The filtrate is mixed with acetic acid, and the zinc precipitated by sulphuretted hydrogen.

The manganese may be precipitated, after neutralization, with an alkaline hypochlorite, or by boiling with an alkaline carbonate.

35. CADMIUM AND ZINC.

The alloy of the two metals is dissolved in hydrochloric acid, the solution, which must be decidedly acid, is largely diluted, and saturated with a slow stream of sulphuretted hydrogen, which precipitates all the cadmium in the form of a yellow sulphide. The latter is thrown upon a weighed filter, and dried at 100° till of constant weight.

It is more accurate to dissolve the sulphide of cadmium in hydrochloric or nitric acid, and to precipitate the oxide of cadmium from the solution, as white carbonate, by means of carbonate of soda. The precipitate is washed, dried and ignited, when it is converted into the brown oxide. Previously to the incineration of the filter, the precipitate should be detached, as far as possible.

The filtrate is boiled to expel the sulphuretted hydrogen, and the zinc precipitated from the hot liquid by carbonate of soda.

Another method of separation consists in decomposing the solution of the two metals by considerable tartaric acid, and then adding caustic soda to distinctly alkaline reaction, dilute with considerable water, and boil for some hours. The cadmium is alone precipitated. The zinc may be precipitated from the filtered solution by sulphide of ammonium.

36. CADMIUM AND COPPER.

Both metals may be precipitated from a weak acid solution by sulphuretted hydrogen, the washed precipitate washed off from the filter, boiled with dilute sulphuric acid, when all the cadmium will be dissolved.

Or the washed precipitate of both metals, with the filter, is dissolved in hydrochloric acid with a little chlorate of potash, the solution saturated with potassa, and then hydrocyanic acid added until the precipitate is again dissolved. From this solution of the double cyanides the cadmium may be precipitated by sulphuretted hydrogen, and the copper will remain. The sulphide of cadmium is treated as in No. 35. The solution of copper is boiled with aqua regia, and while hot the copper precipitated by caustic potassa.

The copper may be separated from cadmium as from zinc, by sulphocyanide of potassium, as in No. 33.

37. GALENITE.

PbS.

The finely-powdered mineral, placed in a capacious dish, is gradually moistened with fuming nitric acid until it is entirely converted into white sulphate of lead; a few drops of sulphuric acid are added, to insure complete conversion, the mass ignited and weighed.

If the residue, previously to ignition, be treated with water, and filtered, only traces of lead are found in the solution. If the galena contain copper, iron, or silver, they will be detected in the solution, the first two by ammonia, and the silver by hydrochloric acid.

If the galena be oxidized with more diluted nitric acid, the residue consists of a mixture of sulphate of lead and sulphur, while the solution contains nitrate of lead, from which the lead may be precipitated by sulphuric acid, or, more completely, by oxalate of ammonia, after neutralization. By igniting the dried residue, the sulphur is volatilized, and sulphate of lead remains.

When boiled with a solution of carbonate of soda, the sulphate of lead is converted into carbonate, which, after washing, is completely dissolved by nitric acid.

Sulphate of lead is dissolved to a great extent by a mixture of tartrate of ammonia and free ammonia. From this solution it may be completely precipitated by sulphide of ammonium as black sulphide of lead, or by chromate of potassa, in the form of yellow chromate of lead.

The sulphate of lead may be reduced to the metallic state by fusion with four times its weight of cyanide of potassium.

38. WHITE LEAD.

$$2\,(PbO, CO_2) + PbO, HO$$

frequently mixed with BaO, SO_3,—CaO, SO_3,—CaO, CO_2, or PbO, SO_3.

Pure white lead is perfectly soluble in dilute nitric acid. The oxide of lead may be determined by ignition, after drying at 100°. In order to estimate the water, a specimen, which has been dried at 100°, is ignited in a tube to which a weighed chloride-of-calcium tube is attached. The carbonic acid, which is expelled at the same time, is determined by loss. White lead sometimes contains a small quantity of basic acetate of lead, indicated by the odor of acetone which is perceived when the specimen is ignited.

White lead adulterated with chalk is likewise dissolved, with exception of traces of impurities, by nitric acid. From the diluted solution, the lead is precipitated by sulphuretted hydrogen, the sulphide of lead collected upon a weighed filter, washed, dried at 100°, and weighed. From the solution, after neutralizing with ammonia, the lime is precipitated by oxalate of ammonia.

If barite be present in the specimen, it is left behind on treatment with nitric acid. After washing and igniting, it is weighed and analyzed as in No. 15.

Gypsum would also be in great measure left behind on dissolving in nitric acid. It may, however, be entirely dissolved and separated from any barite present at the same time, by boiling with a large quantity of dilute nitric acid. The amount of gypsum present may be inferred from that of the sulphate of baryta obtained by precipitating the solution with chloride of barium.

Sulphate of lead would also be left undissolved by dilute nitric acid. After washing, it becomes black when treated with sulphide of ammonium; it is soluble in tartrate of ammonia mixed with free ammonia. In a mixture of sulphate of lead and sulphate of baryta, the former may be converted, by digestion with sulphide of ammonium, into sulphide of lead, which can be transformed into chloride by treatment with concentrated hydrochloric acid, and may then be dissolved out by water.

39. PYROMORPHITE.

$3(3\,PbO, PO_5) + PbCl$.*

In many varieties, the chloride of lead is replaced by chloride of calcium, in others, a part of the phosphoric acid is replaced by arsenic acid. The green varieties contain traces of sesquioxide of iron and sesquioxide of chromium or chromic acid.

Those specimens which are free from lime are finely powdered, and dissolved in caustic potassa. The lead is precipitated from the solution by sulphide of ammonium, filtered, dried, and as much removed from the filter as possible. The filter is then burned and the ashes added to the precipitate, which is then mixed with a little sulphur, strongly heated in dry hydrogen gas, and then weighed as sulphide of lead.

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* May be artificially obtained in crystals, by fusing in a porcelain crucible an intimate mixture of 1 part of fused phosphate of soda, and 7 parts of chloride of lead; the mass is very gradually heated to about the fusing-point of the latter; it is then allowed to cool, and the liquid portion decanted from the crystals.

The filtered solution is acidified with hydrochloric acid, which precipitates any sulphide of arsenic, to be treated as directed in the article upon copper-nickel. (No. 65.)

The liquid filtered from the sulphide of arsenic is concentrated by evaporation, supersaturated with ammonia, and the phosphoric acid precipitated by sulphate of magnesia. (*See* No. 9.)

The chlorine is determined in another portion, by dissolving in nitric acid, and precipitating by nitrate of silver.

For the determination of lime, the mineral is dissolved in nitric acid, and the lead precipitated from the diluted solution by sulphuretted hydrogen. The solution filtered from the sulphide of lead is neutralized with ammonia, and the lime precipitated by oxalate of ammonia. The filtrate is concentrated by evaporation, mixed with ammonia, and the phosphoric acid precipitated by sulphate of magnesia.

Those specimens which are free from lime, but which contain arsenic acid, may be analyzed in the following manner. The mineral, in a state of very fine powder, is digested with moderately dilute sulphuric acid, the greater part of the water evaporated, the mass mixed with alcohol, and the sulphate of lead thrown upon a filter and washed with spirit of wine. The filtrate is evaporated to expel the alcohol, and a stream of sulphuretted hydrogen passed through it, while it is heated to about 50°. It is afterwards allowed to cool while the gas is still passing, and, when saturated with sulphuretted hydrogen, set aside in a closed vessel for twenty-four hours, after which the precipitated pentasulphide of arsenic is filtered off.

The filtered solution is treated with ammonia which precipitates the iron as sulphide, occasionally mixed with a small quantity of sesquioxide of chromium.

The phosphoric acid is precipitated from the filtrate, after concentration, by sulphate of magnesia and ammonia.

In order to separate the sesquioxide of chromium, the mineral is digested with a mixture of concentrated hydrochloric acid and alcohol, the solution filtered, evaporated to expel the alcohol, and the sesquioxide of chromium precipitated from the hot solution by ammonia. It still contains a little phosphoric acid.

40. SILVER AND LEAD.

I. By cupellation.

II. The solution of the two metals in nitric acid is diluted with much water, heated nearly to the boiling-point, and the silver precipitated as chloride of silver by hydrochloric acid. (*See* No. 1.)

The filtered solution is allowed to cool, the greater part of the acid neutralized with ammonia, and the lead precipitated by sulphuretted hydrogen. (*See* No. 39.)

III. The diluted nitric solution of the two metals is mixed with dilute hydrocyanic acid, which precipitates the silver as cyanide. When this has accumulated, leaving the solution clear, it is collected upon a filter which has been dried at 120°, washed, dried at that temperature, and weighed.

From the filtrate, after neutralizing the larger excess of acid, the lead may be precipitated by sulphuretted hydrogen, or if the solution be concentrated by evaporation, by sulphuric acid in the presence of alcohol.

IV. Another method consists in precipitating the solution of the two metals by a slight excess of carbonate of soda, and digesting the precipitate with cyanide of potassium, which dissolves the silver in the form of a double cyanide, leaving the carbonate of lead untouched. Since, however, it contains some alkali, it must be dissolved in nitric acid, and precipitated by sulphuretted hydrogen or sulphuric acid. From the solution containing the silver, the latter may be precipitated as cyanide by nitric acid.

V. The solution of the lead and silver in nitric acid is neutralized with an akali, mixed with an akaline formate, and heated to boiling, when all the silver is precipitated in the metallic state.

41. SILVER AND COPPER.

(Silver-coin.)

The alloy is dissolved in moderately strong nitric acid, the silver precipitated from the hot solution by dilute hydrochloric acid with violent agitation, and the chloride of silver treated as in No. 1.

The oxide of copper is precipitated from the filtrate by caustic potassa at a boiling heat, washed, dried, ignited and weighed, the filter being completely incinerated apart from the precipitate.

If the alloy contain gold also, it is left behind by the nitric acid as a brown powder. If it be present in very small quantities—as, for example, in all old silver coins—the small insoluble residue is filtered off, thoroughly washed, the filter incinerated, and the ash fused before the blowpipe with carbonate of soda, when the gold appears in small globules.

When frequent quantitative determinations of silver are made, as in mints, the test is made either by cupellation, which consists in fusing the weighed alloy with several times its weight of pure lead in a small bone earth cupel in a current of air, when the lead and copper are oxidized and absorbed by the cupel, while the pure silver remains as a fused button. Or, more accurately, by volumetric analysis.

In order to prepare pure silver, it is precipitated from the solution by hydrochloric acid or chloride of sodium, in the form of chloride which is well washed and fused in a porcelain capsule. A fragment of zinc is placed upon the fused mass, and some dilute hydrochloric acid poured over it. After twenty-four hours, the chloride of silver is completely reduced; the spongy masses of silver are rinsed out, rubbed to a fine powder under water, and digested with dilute hydrochloric acid, to remove any zinc. It is then thoroughly washed and fused with borax to a reguline mass.

Or the dry chloride of silver may be mixed with an equal quantity of anhydrous carbonate of soda, and the mixture introduced into a crucible, the bottom and sides of which are coated with as thick a layer as possible of carbonate of soda. The crucible is then heated for a length of time to low redness, and afterwards to the fusing-point of silver.

42. SILVER ASSAY.

From argentiferous galenite tetrahedrite, chalcopyrite, &c., even when intimately mixed with gangue, the whole of the silver, concentrated in a small quantity of lead, may be extracted in the following manner:

One hundred grms. of galenite, finely powdered, are fused with 30 grms. of nitre and 100 grms. of litharge.

Or 1 part of the ore is fused together with 30 to 50 parts of litharge.

Or 1 part of ore may be fused with 3 parts of anhydrous acetate of lead and 2 parts of potashes, under a layer of common salt.

In the button of lead obtained, the silver is determined by cupellation, or in the moist way.

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43. GOLD AND COPPER.

(Coins.)

I. The alloy is dissolved in a mixture of hydrochloric and nitric acids, care being taken that none of the latter shall remain undecomposed after the solution is effected; the liquid is heated with oxalic acid, which precipitates all the gold in the metallic state. For the complete precipitation of the gold, the solution must be dilute, and not contain a large excess of hydrochloric acid, or alkaline chlorides. It is washed, dried, transferred to a porcelain crucible, the filter completely incinerated, and the gold, together with the ashes, ignited and weighed. From the filtrate the copper may be precipitated by sulphuretted hydrogen, or by potassa at a boiling heat.

II. The gold is first precipitated by a solution of pure protosulphate of iron, and the copper is afterwards separated from the solution, either by sulphuretted hydrogen, or by a piece of bright iron placed in the liquid, which must not be too acid, and should be heated nearly to boiling. The precipitated copper is washed, dried, and ignited in air, when it is converted into oxide.

44. GOLD AND SILVER.

I. From an alloy containing less than about 15 per cent. of silver, *aqua regia* dissolves all the gold, while the whole of the silver is left as chloride; for this purpose, however, the metal must be employed in a very thinly laminated state. The solution is evaporated, to expel as much of the nitric acid as possible; and diluted with water, to effect the complete separation of the chloride of silver. From the solution the gold is precipitated by oxalic acid, or by protosulphate of iron.

II. If the alloy contain more than 80 per cent. of silver, pure nitric acid dissolves the whole of the silver, and leaves the gold. Here also the alloy must be thinly laminated. The silver is precipitated by hydrochloric acid. The gold is well washed, and dissolved in *aqua-regia*, to ascertain if any trace of silver be left in it.

III. When the quantity of silver present in the alloy is between 15 and 80 per cent., it cannot be entirely extracted by nitric acid, neither can all the gold be dissolved out by *aqua regia*, since the metal becomes covered with a thick layer of chloride of silver. Such an alloy should be fused in a porcelain crucible with 3 times its weight of pure lead. From this alloy, nitric acid then dissolves all the lead and silver, leaving pure gold.

From the solution filtered from the gold, the silver is precipitated by hydrocyanic acid; or, after diluting largely, and heating nearly to boiling, by hydrochloric acid.

IV. Silver and gold in alloys of these metals may also be separated by concentrated sulphuric acid, whatever may be the relative proportion of the two metals. The thinly laminated alloy is heated with the acid in a capacious dish, until all evolution of gas ceases, and the acid begins to evaporate. The sulphate of silver which is produced is then dissolved in the requisite quantity of hot water, and the solution decanted from the gold, which, for greater certainty, is once more heated with a small quantity of sulphuric acid; afterwards thoroughly washed, ignited, and weighed.

V. All such alloys may be also conveniently analyzed by fusion with bisulphate of potassa.

45. AMALGAMS.

The following amalgams may be analyzed by heating very gradually in a porcelain crucible, finally raising the heat to redness, till the mercury is entirely volatilized, and the tin or copper oxidized. To insure complete oxidation, the mass is ultimately moistened with concentrated nitric acid, and again ignited. The amalgam of silver leaves the latter in the metallic state. In order to estimate the mercury also directly, the following method is adopted:—

I. AMALGAM OF COPPER.*—The amalgam is dissolved in *aqua regia*, the solution neutralized, though not completely, with potassa, mixed with formate or sulphite of potassa or soda, and allowed to stand for some time at a temperature between 50° and 60°. All the mercury is thus precipitated as subchloride. Above 60°, metallic mercury would also be separated. The subchloride of mercury is collected upon a filter, which has been dried at 100° and weighed, and its weight determined after drying at 100°.

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* This amalgam, which is semi-fluid at 100°, but solid and crystalline at the ordinary temperature, is obtained when copper, which has been precipitated by zinc, is moistened with nitrate of suboxide of mercury, and triturated in a warm mortar with mercury, added by degrees, until the amalgam has the consistence of butter.

From the filtered solution the oxide of copper is precipitated, at a boiling heat, by caustic potassa.

II. Amalgam of Tin (amalgam for mirrors).—This is dissolved in *aqua regia*, the solution mixed with ammonia in slight excess, afterwards with an excess of sulphide of ammonium, and digested for a long time in a closed vessel. The bisulphide of tin which is formed dissolves in the sulphide of ammonium, and the black sulphide of mercury separates; it is collected upon a weighed filter, washed with weak sulphide of ammonium, and dried at 100°.

From the solution in sulphide of ammonium the bisulphide of tin is precipitated by dilute hydrochloric acid, filtered off, washed, dried, and roasted, together with the filter, in a porcelain crucible, with free access of air. A gentle heat is at first applied, which is gradually increased, till the whole of the precipitate is converted into white binoxide of tin; a fragment of carbonate of ammonia is held in the ignited crucible at the end of the operation.

III. Amalgam of Silver.*—The amalgam is dissolved, by the aid of heat, in nitric acid, so that the solution may contain the whole of the mercury in the state of protoxide; the acid solution is diluted with water, and the silver precipitated by an excess of hydrochloric acid.

The mercury in the filtrate from the chloride of silver may be precipitated by phosphorous acid.

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* May be obtained in crystals by allowing a small quantity of mercury to remain in a moderately diluted solution of nitrate of silver, or by placing a thick bright copper-wire in the mixed solutions of nitrate of silver and of suboxide of mercury.

46. MIXTURES OF PROTOXIDE OF MERCURY, MINIUM, AND CINNABAR.

By digesting with dilute nitric acid, the protoxide of mercury is extracted, together with a portion of the protoxide of lead, the remainder of the lead being left behind in the form of brown binoxide, mixed with the cinnabar. This residue is well washed upon a weighed filter.

From the solution, which must contain an excess of nitric acid, the lead is precipitated by an excess of sulphuric acid, and a little alcohol. The mercury may then be precipitated as protochloride by hydrochloric acid and phosphorous acid. Before the separation of the lead these last two reagents would have given chloride of lead with the protochloride of mercury.

The mixture of cinnabar and binoxide of lead is treated, upon the filter, with a warm mixture of dilute nitric acid and a little oxalic acid, which dissolves the binoxide of lead, with evolution of carbonic acid. The cinnabar is then washed, dried at 100°, and weighed.

The lead is precipitated from the solution by sulphuric acid, with addition of some alcohol.

In order to analyze the cinnabar, it is dissolved (in this case, together with the filter) in concentrated hydrochloric acid, with careful addition of chlorate of potassa; the sulphuric acid is then precipitated from the diluted solution by chloride of barium, the filtrate concentrated, and the mercury precipitated by protochloride of tin, or, better, by phosphorous acid.

47. TIN AND COPPER.

(Bronze, Gun-metal, Bell-metal.)

I. The alloy, as finely divided as possible, is oxidized with concentrated nitric acid, the greater excess of the latter evaporated, the solution diluted with hot water, and the undissolved binoxide of tin filtered off. The copper is precipitated from the filtrate by caustic potassa, at a boiling-heat.

If the bronze contain also zinc, lead, and iron, the lead is precipitated by sulphuric acid, and the copper by sulphuretted hydrogen. The solution filtered from the sulphide of copper is heated with some chlorate of potassa in order to peroxidize the iron, and the sesquioxide of the latter metal precipitated by an excess of ammonia. The oxide of zinc remains dissolved in the alkali, and is precipitated by sulphide of ammonium. Or the method described in No. 31 may be followed.

II. A surer method of obtaining the binoxide of tin free from other metals consists in oxidizing the alloy with nitric acid, evaporating to complete dryness, moistening with hydrochloric acid, and after some time adding water, the mass dissolves completely and the binoxide of tin is precipitated by sulphuric acid. After it has fully settled, it is filtered, washed, and ignited.

III. A very accurate analysis may also be effected by heating the alloy in a current of dry chlorine, when the tin and a part of the iron are volatilized as chlorides, which are conducted into water, and chloride of copper, chloride of zinc, and chloride of lead are left. (*See* Tetrahedrite.)

48. TIN AND LEAD.

(Pewter, Soft Solder.)

The alloy is oxidized with moderately strong nitric acid, which leaves the tin undissolved in the form of binoxide; after heating and diluting with water, the binoxide of tin is filtered off, washed, dried, and ignited.

From the filtrate the lead is precipitated by dilute sulphuric acid. The whole solution, containing the suspended precipitate, is evaporated to expel the nitric acid, until the sulphuric acid begins to volatilize; it is then diluted with water, and the sulphate of lead collected upon a weighed filter, which has been dried at 120°, and washed with spirit of wine. A filter which has not been weighed may be employed, if care be taken to remove as much as possible of the precipitate from the filter, and to incinerate the latter carefully apart, so that no reduction of lead may take place. (Moreover, *see* No. 49.)

After the above operation it is difficult to obtain the binoxide of tin perfectly free from lead. It is much surer to fuse the alloy with a mixture of carbonate of potassa and sulphur, to extract the tin as a sulphide, and proceed as in No. 49.

49. BISMUTH, LEAD, AND TIN.

The alloy is oxidized with moderately strong nitric acid, the mass mixed with an excess of ammonia and sulphide of ammonium, and digested for some time in a closed flask. In this way the tin is entirely dissolved as a sulphur-salt. The solution is filtered off from the other sulphides, which are then washed with very weak sulphide of ammonium, and dried.

From the solution the bisulphide of tin is precipitated by dilute hydrochloric acid, filtered off, washed, and dried. It is then gradually heated, together with the filter, in a porcelain crucible, with free access of air; at first gently, and ultimately to redness, so that it may be entirely converted into binoxide of tin. A fragment of carbonate of ammonia is held in the crucible at the end of the operation, to remove any sulphuric acid which may have been formed.

The mixture of sulphide of bismuth and sulphide of lead is detached, as far as possible, from the filter, the latter incinerated, and the ash added to the precipitate which is then oxidized in a capacious capsule, with concentrated nitric acid, a little sulphuric acid added lest there should not be sufficient, and the excess of nitric acid expelled by heat. The mass is then treated with a little water, the solution of sulphate of bismuth filtered off from the sulphate of lead, the latter washed with water containing sulphuric acid, dried, and ignited.

From the filtrate the teroxide of bismuth is precipitated by carbonate of ammonia in excess; the liquid is digested for some time to insure the complete separation of the precipitate, which is then filtered off, washed, detached as far as possible from the filter, and ignited in a porcelain crucible, when it is converted into yellow teroxide of bismuth. The filter is incinerated separately.

If the oxide is fused with cyanide of potassium, it is reduced and determined as metallic bismuth.

The best method to separate bismuth from the other metals depends upon this, that by the addition of a large quantity of water to the hydrochloric acid solution, there is obtained a perfectly insoluble precipitate of basic chloride of bismuth ($2\,Bi_2\,O_3 + Bi_2\,Cl_3$), that may be weighed in this state, or reduced to a metallic state, by fusing with cyanide of potassium. In order to separate the lead, the concentrated solution is mixed with so much hydrochloric acid that the chloride of lead is precipitated, and the addition of a few drops of water causes no turbidity. Dilute sulphuric acid is then added, allowed to stand for some time, stirring occasionally, then mixed with alcohol, well stirred, and the sulphate of lead left to settle down. It is then filtered, washed with alcohol containing hydrochloric acid, and afterwards with pure alcohol. The filtered solution is then mixed with a large quantity of water, when the bismuth is precipitated as basic chloride.

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50. BISMUTH AND COPPER.

By carbonate of ammonia bismuth is precipitated, while copper remains in solution, but the separation is only approximate. It is more accurate to precipitate the bismuth as basic chloride, as in No. 49.

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51. SCHWEINFURT GREEN.

$$CuO, \bar{A} + 3\,(CuO, AsO_3).$$

When this substance is heated with caustic potassa the acids are extracted, and red suboxide of copper left, one-third of the arsenious acid being converted into arsenic acid.

If the filtered liquid be neutralized with nitric acid, and nitrate of silver gradually added, a red brown precipitate of arseniate of silver is first produced, and afterwards a yellow precipitate of arsenite of silver.

In order to separate the two acids, the solution, previously acidified with nitric acid, is mixed with excess of ammonia, and sulphate of magnesia added, which has been mixed with so much chloride of ammonium that it is no longer precipitated by ammonia. The arsenic acid is thus precipitated by arseniate of magnesia-ammonia. After the lapse of twelve hours, the precipitate is collected upon a dried and weighed filter, washed with dilute ammonia, and thoroughly dried, at 100°. It then has the composition $2\,MgO, NH_4\,O, AsO_5 + HO$, and contains 60.53 per cent. of arsenic acid.—It is not safe to ignite this precipitate, since arsenic is then liable to be reduced and volatilized.

The solution filtered from the magnesia-precipitate is acidified with hydrochloric acid, and the arsenious acid precipitated as tersulphide of arsenic.

If the alkaline solution is saturated with hydrochloric acid, and heated with sulphurous acid, the arsenic acid is reduced to arsenious acid and may be precipitated by hydrosulphuric acid. Or if the solution is saturated with chlorine gas, all the arsenious acid will be converted into arsenic acid, and may then be precipitated by the ammoniated salt of magnesia.*

If the original pigment be digested with a mixture of concentrated hydrochloric acid and alcohol, a solution of chloride of copper is obtained, and the arsenious acid remains behind as a white powder.

By long digestion with an excess of sulphide of ammonium, the copper is separated as sulphide, while all the arsenic is dissolved and may be precipitated as tersulphide of arsenic by adding hydrochloric acid to the filtrate.

When Schweinfurt green is distilled with dilute sulphuric acid, the acetic acid passes over, and may be converted into acetate of baryta by adding that base. The accurate quantitative estimation of the acetic acid can only be effected by ultimate organic analysis.

52. ARSENIC AND LEAD.

The alloy, in a fine state of division, is oxidized with nitric acid, the excess of acid evaporated, the solution neutralized with ammonia, and the precipitated white mass digested for some time with an excess of sulphide of ammonium in a closed vessel. The solution of sulphide of arsenic is filtered from the sulphide of lead, which is collected upon a weighed filter, washed, first with weak sulphide of ammonium, then with water, dried and weighed, and treated as in No. 39.

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* The detection and separation of arsenic, see the following article, also poisoning by arsenic.

The sulphide of arsenic is precipitated from the solution by dilute hydrochloric acid, the sulphuretted hydrogen expelled by a gentle heat, the precipitate filtered off, washed, and gently heated, together with the filter, in a beaker, with concentrated hydrochloric acid, with gradual addition of chlorate of potassa, until all the arsenic and part of the sulphur are oxidized and dissolved. The solution is diluted with water, passed through a filter, which must be well washed, and the arsenic acid precipitated, as in No. 51, with sulphate of magnesia and ammonia.

53. ARSENIC AND TIN.

The finely-divided compound is gradually and carefully oxidized with nitric acid, which is dropped upon it in a weighed vessel. When it is converted into a dry white mass, more nitric acid is added, and the whole evaporated to perfect dryness in a water-bath. The mass dried at 100° is weighed. A portion of it is then weighed in a bulb-tube, one limb of which is bent downwards, and dips into caustic ammonia contained in a small flask. A stream of sulphuretted hydrogen is passed through the bulb-tube, and when it is filled with gas, the mass is heated, gently at first, afterwards more strongly, until a sublimation takes place of sulphide of arsenic and sulphur, which dissolve in the ammonia. When no fresh sublimate is formed, the apparatus is allowed to cool, and the piece of tube cut off in which any sublimate still remains. This tube is placed in warm solution of potassa, which easily dissolves the sublimate, the solution added to the sulphide of ammonium, and the whole liquid carefully acidified with hydrochloric acid which precipitates the sulphide of arsenic. Some powdered chlorate of potassa is added to the liquid, without filtering, and heat applied till there remains only pure sulphur, which is filtered off. From the filtrate, the arsenic acid is then precipitated by ammonia and sulphate of magnesia as in No. 51.

All the tin is left in the bulb in the form of dark brown bisulphide of tin, mixed, however, with a variable quantity of sulphur, so that the amount of tin cannot be immediately inferred from the weight of the residue. In order to determine the tin, the contents of the bulb are thrown into a porcelain crucible, moistened with nitric acid, and ignited, with access of air, until the tin is entirely converted into white binoxide, which is then weighed. The quantities of tin and arsenic are afterwards calculated for the whole quantity of the original oxidized mass.

A simpler method is based upon the solubility of sulphide of arsenic in bisulphate of potassa, while the sulphide of tin is insoluble. The mass oxidized by nitric acid is digested with a solution of caustic potash and sulphur until it is completely dissolved (or with the exception of a basic sulphide, from which it may be filtered). The solution is then mixed with an excess of sulphurous acid, digested, and boiled until about two-thirds of the water has evaporated and all the sulphurous acid. The sulphide of tin is filtered off and washed with a concentrated solution of common salt, and not with water. This may then be separated from the precipitate by a solution of acetate of ammonia slightly acid, but the liquid must not be mixed with the salt washings. The sulphide of tin is dried and converted into the oxide by roasting in the air. The rsenic contained in the fluid as arsenious acid, is precipitated by a stream of sulphuretted hydrogen.

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54. TARTAR-EMETIC.

$$KO\bar{T}, SbO_3\,\bar{T} + 2\,HO.$$

The powdered salt loses all its water at 100°.

The substance is dissolved in about 300 times its weight of warm water, and the solution saturated with sulphuretted hydrogen. Some hydrochloric acid is afterwards added to promote the separation of the tersulphide of antimony; when the liquid has become clear, the precipitate is collected upon a weighed filter, well washed, dried at 150°, and weighed. In this case the weight of the antimony may be at once inferred from that of the precipitate.

The filtrate is evaporated to dryness, the saline residue heated till the tartaric acid is completely carbonized, the carbonaceous mass digested with dilute hydrochloric acid, filtered off and thoroughly washed. The solution is evaporated, and the residual chloride of potassium gently ignited in a covered crucible, and weighed.

The amount of the tartaric acid is inferred from the difference. It can be directly determined only by ultimate organic analysis.

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55. ANTIMONY AND LEAD.

(Type Metal.)

The finely-divided compound is oxidized with nitric acid, the solution mixed with ammonia in slight excess, and afterwards with an excess of yellow sulphide of ammonium, with which it is digested for some time until the precipitate is perfectly black. The solution is then diluted with water, the sulphide of lead collected upon a dried and weighed filter, thoroughly washed with dilute sulphide of ammonium, and afterwards with water, dried at 150°, and weighed. (*See* No. 39.)

The sulphide of antimony is precipitated from the solution by dilute sulphuric acid, and the liquid exposed to the air until most of the sulphuretted hydrogen has been dissipated. The precipitate is then thrown upon a dried and weighed filter, well washed, and dried at 100° till its weight is constant.

Since the quantitative composition of this precipitate is not accurately known, and since, moreover, it contains some free sulphur, it must now be analyzed, and either the sulphur or the antimony in it determined.

To determine the amount of sulphur which it contains, a weighed quantity is detached from the filter and oxidized, very gradually and cautiously, in a flask, with concentrated nitric acid. Concentrated hydrochloric acid is afterwards added, and the mixture digested until all the antimony and all the sulphur are dissolved. As soon as this is the case, so much tartaric acid is added, that the solution may be diluted with water without any precipitation taking place. If any sulphur should have been separated in an unoxidized state, it must be collected upon a weighed filter. The sulphuric acid is then precipitated from the diluted solution by chloride of barium, and the precipitate washed with hot water. The quantity of sulphur, and, in consequence, that of the antimony, are calculated for the total weight of the precipitated sulphide of antimony.

For the direct estimation of the antimony, a weighed portion of the original precipitate is introduced into a weighed bulb-tube, and heated in a stream of hydrogen gas, at first very gently, and ultimately to the fusing point of the antimony, from which the sulphur is thus completely separated.

Or, instead of the hydrogen, a stream of carbonic acid gas free from air may be passed through the tube, and the precipitate heated in it until it does not lose any more sulphur, and is converted into black tersulphide of antimony.

A more accurate method consists in converting the sulphide of antimony into the antimoniate of the oxide of antimony (Sb_2O_3, Sb_2O_5), complete oxidation being produced by fuming nitric acid. To prevent too rapid action it should be moistened first with a few drops of weak acid.

The oxidation is made in a weighed porcelain crucible. By digesting for some time the decomposition is complete, and the pulverulent precipitate of sulphur separates. The acid is then carefully evaporated and the residue ignited.

56. BOURNONITE.

$$3\,Cu_2S, Sb_2S_3 + 2\,(3\,PbS, Sb_2S_3).$$

The powdered mineral is gradually and carefully oxidized with concentrated nitric acid, the mass mixed with ammonia, and digested for some time, in a closed vessel, with yellow sulphide of ammonium. The solution is then treated as directed in No. 55.

The residue containing sulphide of copper and sulphide of lead is dried in the funnel, detached as far as possible, from the filter, the latter incinerated, and the sulphides afterwards oxidized, in a dish, by the gradual addition of fuming nitric acid. Some sulphuric acid is then added, the whole of the nitric acid expelled by heat, and the sulphate of copper extracted from the mass by water. The sulphate of lead is washed, dried, and ignited. The oxide of copper is precipitated from the solution by caustic potassa, at a boiling heat.

This method is not quite accurate, since a little sulphide of copper dissolves in the sulphide of ammonium together with the tersulphide of antimony; sulphate of lead, moreover, is not quite insoluble. The determination of the lead is more accurate if all free sulphuric acid be expelled by heat before the sulphate of copper is extracted with water.

A more exact method for the analysis of this mineral is that with chlorine, described in the article upon Tetrahedrite.

57. ZINKENITE.*

PbS, Sb_2S_3.

The amount of sulphur present may be inferred from the loss which the compound suffers when heated ~~in~~ a bulb-tube, through which a stream of hydrogen is passed, when all the sulphur is evolved as sulphuretted hydrogen, and PbSb remains behind.

The relative proportions of lead and antimony are determined as in No. 55.

For the direct estimation of the sulphur, the finely-divided compound is mixed with 3 parts of chlorate of potassa, and 3 parts of carbonate of soda, and heated in a porcelain crucible, at first gently, and ultimately to redness, until the chlorate of potassa is completely decomposed. The salts are then extracted from the mass with water, the residue well washed, the solution acidified slightly with hydrochloric acid, and the sulphuric acid precipitated by chloride of barium.

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* Plagionite jamesonite, and feather-ore, are similar combinations. Zinkenite may be easily prepared artificially by fusing together 7½ parts of sulphide of lead, with 11 parts of black tersulphide of antimony in a glass tube.

58. BERTHIERITE.

FeS, Sb_2S_3.

The mineral, in the state of fine powder, is oxidized with hydrochloric acid and chlorate of potassa, until the separated sulphur has a pure yellow color. The solution is mixed with tartaric acid, and may then be diluted with water without any precipitation taking place. The separated sulphur is collected upon a dried filter, washed, and dried at 100°. The sulphuric acid produced by the oxidation is precipitated from the solution by chloride of barium, and the sulphate of baryta washed with hot water.

When the excess of baryta has been removed from the filtrate by sulphuric acid, a stream of sulphuretted hydrogen gas is passed through the solution, and the antimony precipitated. (*See* also No. 55.)

From the filtered liquid the iron is completely oxidized and then precipitated by ammonia.

59. RED SILVER-ORE.*

Pyrargyrite, $3AgS, Sb_2S_3$. Proustite, $3AgS, As_2S_3$.

1. PYRARGYRITE.—To determine the amount of sulphur, a weighed quantity of the mineral is fused in a

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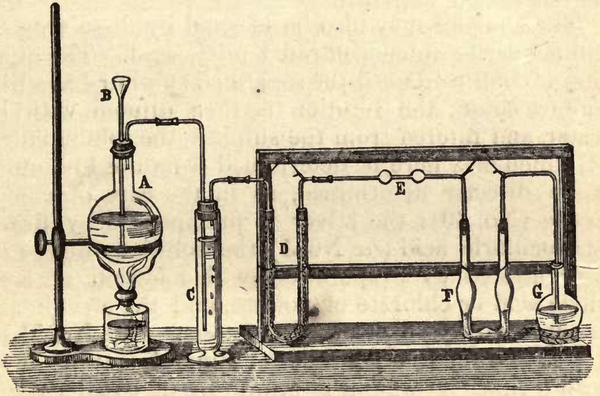
* These compounds may be readily obtained artificially by fusing their constituents together. That which contains antimony is prepared by fusing 2·2 parts of sulphide of silver with 1 part of black tersulphide of antimony in a crucible, beneath a layer of

bulb-tube, over a large spirit-lamp or gas-burner, in a stream of dry hydrogen, as long as any sulphuretted hydrogen is formed; all the sulphur is thus expelled, in combination with hydrogen. The conclusion of the operation is also indicated by a sort of coruscation which takes place, and the antimonide of silver is left in the form of a perfectly bright, smooth, movable globule.

The tube is allowed to cool slowly, weighed, and placed in communication with an apparatus for the evolution of chlorine, in a current of which the antimonide of silver is fused, until no more pentachloride of antimony is volatilized, and pure fused chloride of silver remains. The latter is then treated as in the case of gray copper-ore.

Fig. 11.



The antimonide of silver may also be oxidized by

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common salt; to prepare the arseniferous compound, 3 parts of sulphide of silver and 1 part of yellow tersulphide of arsenic, or 32.4 parts of powdered silver 9.6 parts of sulphur, and 7.5 parts of arsenic are fused together in a glass tube closed at one end. Combination takes place with incandescence.

nitric acid, and the silver and the antimony separated by sulphide of ammonium, as in antimonide of lead (No. 55.)

2. PROUSTITE.—The light colored variety, when fused in a current of hydrogen, loses all its sulphur and arsenic; but the complete expulsion of the latter can scarcely be effected in a glass tube. The experiment must be conducted in a small porcelain boat, placed in a porcelain tube. After a certain time, the fused substance suddenly swells up to a voluminous bladder-like mass, from which the last portions of arsenic can be but slowly expelled.

The analysis may also be effected by dissolving the red silver-ore in concentrated nitric acid. The digestion is continued until the separated sulphur has a pure yellow color; the solution is then diluted with hot water, and filtered from the sulphur, the total quantity of which may here be determined from the loss, unless it be directly determined, as in the case of chalcopyrite (No. 30); the silver is precipitated by diluted hydrochloric acid (*see* No. 1), the solution filtered off, concentrated by evaporation, with addition of some nitric acid or chlorate of potassa, and the arsenic acid precipitated by sulphate of magnesia. (*See* No. 51.)

Or the very finely-powdered mineral may be fused with 5 times its weight of a mixture of equal parts of nitre and carbonate of soda in a platinum crucible, at the bottom of which a layer of carbonate of soda has been placed. The mass is afterwards dissolved out with hot water, the silver filtered off, washed, ignited and weighed. The solution is acidified with hydrochloric acid, mixed with ammonia, and the arsenic acid precipitated by sulphate of magnesia. The amount of sulphur is determined by loss, unless it be precipitated from the original solution in the form of sulphate of baryta, when it must be very carefully washed with hot water to free it from the nitrate of baryta which it carries down.

Both compounds may also be analyzed with great accuracy by means of chlorine gas, as described in the article upon Grey Copper-ore, or Tetrahedrite.

In analyzing a mixture of light and dark red silver-ore, the arsenic and antimony are separated according to the method described in No. 61.

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60. TIN AND ANTIMONY.

The weighed compound is dissolved in hydrochloric acid, with gradual addition of nitric acid, and a piece of pure tin placed in the solution, with which it is heated for some time, until the whole of the antimony is precipitated; the latter is collected upon a weighed filter, washed, dried at 100°, and weighed; the amount of tin is inferred from the difference.

In order to determine both metals directly, the compound, as finely divided as possible, is oxidized in a beaker with strong pure nitric acid, the mass evaporated to dryness, gently ignited, and fused, in a silver crucible, with a large excess of hydrate of soda. When cool, the mass is treated with water, rinsed out into a beaker, and the solution mixed with $\frac{1}{3}$ its volume of strong alcohol. The insoluble antimoniate of soda is thus separated from the stannate, carbonate, and excess of hydrate of soda, which are dissolved by the weak spirit. When the liquid has become perfectly clear, the precipitate is filtered off, and washed, first with a mixture of equal volumes of alcohol and water, and finally with strong alcohol.

The alkaline solution is heated to expel the alcohol, diluted with water, acidified with dilute sulphuric acid, and the tin precipitated by sulphuretted hydrogen

The bisulphide of tin is then converted into binoxide of tin, as directed in No. 49.

The antimoniate of soda is detached as far as possible from the filter, and a mixture of hydrochloric and tartaric acids poured over the latter, and allowed to flow into the beaker containing the remainder of the precipitate. When the salt is perfectly dissolved, and the filter has been washed, the antimony is precipitated by sulphuretted hydrogen. The antimony contained in the precipitate is determined as in No. 55.

The antimoniate of soda may also be collected upon a weighed filter, dried at 100°, and a weighed portion mixed with sal-ammoniac in a porcelain crucible, and ignited, when all the antimony is volatilized, and the salt converted into chloride of sodium. The operation must be repeated several times till the weight is constant, and the amount of the antimony may be calculated from that of the chloride of sodium obtained.

Or the dried antimoniate of soda may be fused in a porcelain crucible with an excess of cyanide of potassium. The antimony is reduced and collects in a metallic button.

61. ARSENIC AND ANTIMONY.*

If only these two metals be present, as in native arsenic, a complete separation may be effected by heating the compound in a bulb-tube through which a stream of dry carbonic acid gas is transmitted, when the whole of the arsenic is volatilized, and the antimony remains behind. If too strong a heat be applied, a portion of the latter metal may also be volatilized.

When the compound under examination contains, as is often the case, the two metals in the form of sulphides, they may be at least approximately separated by digestion with concentrated hydrochloric acid, which dissolves the sulphide of antimony, and leaves that of arsenic, or with carbonate of ammonia, which dissolves the sulphide of arsenic.

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* See No. 132. Poisoning by Arsenic.

Methods for Quantitative determination.

I. The compound is carefully oxidized with *aqua-regia*, or with hydrochloric acid and chlorate of potassa, some tartaric acid and a considerable quantity of chloride of ammonium added, and the mixture then treated with ammonia in excess, which must dissolve the whole. From this solution the arsenic acid is precipitated by sulphate of magnesia. (*See* No. 51.)

The filtrate is acidulated with hydrochloric acid, and the antimony precipitated by sulphuretted hydrogen, and treated as in No. 54.

II. A more accurate method depends upon the fact that freshly precipitated sulphide of arsenic is soluble in sulphite of potassa and sulphurous acid, while the sulphide of antimony is not.

The analysis of commercial gray sulphide of antimony or metallic antimony, is made in the following manner:—

The very finely pulverized and weighed substance is digested with a solution of sulphide of potassium and some sulphur, until it is dissolved. There generally remains a black mixture of sulphides of lead, iron, and copper, which are separated by filtration and analyzed by themselves. The solution is then mixed with a large excess of a saturated solution of sulphurous acid in water, with this digested and kept at the boiling-point until two-thirds of the water has evaporated, and all the sulphurous acid is driven off. The precipitated sulphide of antimony is filtered, washed, and treated as in No. 54. From the solution which contains the arsenic as arsenious acid, it is precipitated by hydrosulphuric acid as in No. 52.

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62. ARSENIC, ANTIMONY, AND TIN.

The compound is divided as finely as possible, and carefully oxidized with strong and pure nitric acid, the mass evaporated to dryness and fused in a silver crucible with eight times its weight of hydrate of soda, the evaporating vessel being previously rinsed with solution of soda, which is added to the contents of the crucible and evaporated to dryness. The fused mass is treated with hot water, then diluted with water, and one-third its volume of strong alcohol added. The mass is allowed to stand for twenty-four hours and frequently stirred; the antimoniate of soda is then filtered off, and washed first with a mixture of 2 vols. of water and 1 vol. of alcohol, next with a mixture of equal vols., and lastly with a mixture of 3 vols. of alcohol and 1 vol. of water, adding to each a few drops of solution of carbonate of soda. The washed salt is treated as in No. 60.

The alkaline filtrate is supersaturated with hydrochloric acid, which produces a bulky precipitate of arseniate of binoxide of tin. Without filtering this off, the liquor is saturated with sulphuretted hydrogen, the precipitate thus converted into a dark brown mixture of bisulphide of tin and tersulphide of arsenic, and the liquor then allowed to stand for twenty-four hours in the closed vessel. The precipitate is now collected on a weighed filter and dried at 100°. The separation of the tin and arsenic is effected by heating in sulphuretted hydrogen, as in No. 53.

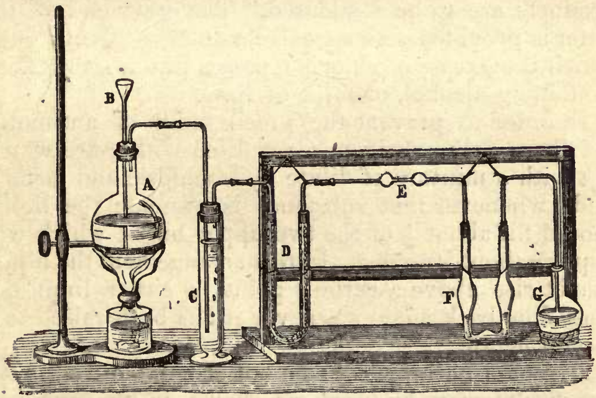
A weighed portion of the entire precipitate might also be mixed with about 12 times its weight of a mixture of 3 parts of carbonate of soda and 1 part of cyanide of potassium, and heated in a covered porcelain crucible until all the arsenic is driven off. On treating the residue with water, the tin would be left behind in the metallic state. Or the mixture could be heated in a long glass tube, in a slow current of carbonic acid gas, and thus the arsenic obtained as a sublimate in the tube. In order to secure a more complete condensation, a weighed coil of fine sheet copper could be introduced into the tube, and heated to ignition at one place for the purpose of forming arsenide of copper.

63. TETRAHEDRITE.

$$4\,(Cu, Ag, Fe, Zn, Hg), + (Sb_3, As, Bi)_2\,S_3.$$

Every specimen of tetrahedrite does not contain all these constituents; some of them may be entirely

Fig. 12.



absent, and generally they may replace each other in the different kinds in varying quantities.

The analysis is best effected by gently heating the mineral in dried chlorine gas, when sulphur, arsenic, antimony, mercury, and a portion of the iron are volatilized in the form of chlorides, and copper, silver, zinc, and part of the iron remain behind, likewise converted into chlorides.

The above figure shows the construction of the apparatus to be used in such analyses. The chlorine gas, for the purpose of drying it, is first passed through a small cylinder containing concentrated sulphuric acid, and thence through the chloride-of-calcium-tube, which is fixed upon a wooden stand.

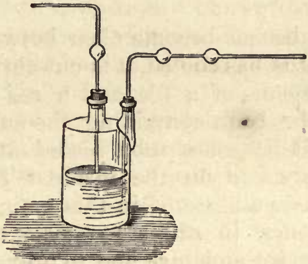
The mineral, finely divided, is weighed in the bulb-tube. The latter is best provided with two bulbs, in order to collect the greater portion of the sublimate in the second bulb, and thus to prevent the tube from being stopped up.

The end of the tube bent downwards is connected by means of a good cork or a caoutchouc tube, with the three-bulb-tube or receiver, in which the volatile products are to be condensed. The other end of the latter is provided with a small conducting tube, through which the excess of chlorine passes into a small flask containing alcohol, or milk of lime.

In order to prevent the precipitation of antimony, the three-bulb receiver is not filled with pure water, but with a mixture of dilute hydrochloric and tartaric acids, whenever that substance is present; the liquid should fill about ⅓ of the two upper bulbs, which will require about 50 grms. In this arrangement the liquid cannot rise above a certain point in either limb, but must flow back again whenever it has been raised to a certain height.

If such a bulb-receiver be not at hand, a flask with two necks may be used, as shown in the annexed figure. The perpendicular limb of the bulb-tube almost touches the mixture of acids in the receiver, but does not dip into it, because the liquor might in that case recede into the bulb-tube, the chlorine being rapidly absorbed. The conducting-tube, inserted through the second neck, expands at its upper portion into a bulb, and is cut off below in an oblique direction; it enters the liquid so far, that this can be pressed up into the bulb only, and must then flow back again. To this tube a second one is attached, which is bent at a right angle, and conducts the excess of chlorine into alcohol, or milk of lime.

Fig. 13.



It is advisable not to connect the bulb-tube, containing the mineral, with the chlorine apparatus, until most of the atmospheric air has been expelled from it.

The complete decomposition of tetrahedrite takes place even at the ordinary temperature, with strong evolution of heat. When the bulb has nearly cooled again, it is heated gently by a very small flame, in order to separate the volatile products from the non-volatile, and to drive the former into the second bulb. It is scarcely possible to drive off all the sesquichloride of iron; the heating is therefore discontinued as soon as vapors of this compound only appear to be evolved.

The chlorine gas is to be passed through in a gentle current only, especially towards the last, when the sublimation is effected, because otherwise the vapors of the volatile products may pass unabsorbed through the receiver.

When the tube has become clear between the bulbs, and the apparatus has cooled, it is cut through between the bulbs by means of a file and a red-hot coal, and the end with the bulb containing the sublimate is covered with a short glass tube, sealed at one end and moistened with water on the inside. The tubes are allowed to remain connected in this manner for at least twenty-four hours, in order to cause the sublimate gradually to attract moisture and to prevent its becoming hot and thus occasioning loss on being afterwards dissolved in water, as would otherwise be the case. It is then dissolved in a little water, to which some hydrochloric and tartaric acids have been added, the tube is carefully rinsed, and the rinsings added to the solution in the receiver. Should the liquid be cloudy, in consequence of a separation of antimonious acid, a gentle heat must be applied, in order to redissolve the latter. In case of sulphur having separated in an unoxidized state, it must be filtered off.

I. Analysis of the Fixed Residue.—The bulb containing it is placed in a beaker with dilute hydrochloric acid, and digested until the contents are dissolved, with the exception of the chloride of silver. This is filtered off and treated as in No. 1. Should chloride of lead be present, as is the case in the analysis of bournonite, it must be dissolved by using a larger quantity of water. In this case the contents of the bulb have to be heated very cautiously, that the chloride of lead may not volatilize.

A slow current of sulphuretted hydrogen is then passed through the solution until it is completely saturated. The precipitated sulphide of copper is treated as in No. 30, or, if lead be present, as in No. 56.

The solution filtered off from the precipitate contains part of the iron, and if too great a heat was avoided, all the zinc; it is then heated to ebullition, and mixed with some chlorate or hypochlorite of an alkali, in order to convert the former metal into a higher oxide; the iron and zinc are then separated and determined as in No. 31.

II. ANALYSIS OF THE VOLATILE PRODUCTS.—This solution contains the mercury, antimony, arsenic, a portion of the iron, and the sulphur, partly in the form of sulphuric acid, partly unoxidized.

The sulphuric acid can be precipitated with chloride of barium, and the excess of baryta again removed by sulphuric acid.

It is, however, much more convenient to determine the amount of sulphur in a separate portion of the mineral. For this purpose it is finely divided, mixed with three times its weight of finely-powdered chlorate of potassa and then with as much of dry carbonate of soda, and the mixture very gradually heated in a platinum crucible (the bottom of which is previously covered with carbonate of soda, as a precaution) until all the chlorate of potassa is decomposed. When cold, the mass is treated with water, the solution filtered, slightly acidulated with hydrochloric acid, and the sulphuric acid precipitated by chloride of barium as in No. 3.

For the determination of the other constituents, the solution of the volatile chlorides is heated to about 60° and then a gentle current of sulphuretted hydrogen passed through it until it is cold. When completely saturated with sulphuretted hydrogen, the solution is allowed to stand for twelve hours, and then the precipitate, which consists of the sulphides of mercury, antimony, and arsenic; collected on a filter which has been dried and weighed. After being washed with sulphuretted-hydrogen water, the precipitate is removed from the filter, taking care not to damage the latter; it is washed off as well as possible, and a concentrated solution of sulphide of ammonium poured upon it, with which it is digested in a closed vessel until the whole of the sulphides of arsenic and antimony are dissolved, and the sulphide of mercury has assumed a pure black color. When completely cold, it is again collected on the filter previously used, washed first with dilute sulphide of ammonium, and towards the end with pure water, dried and weighed.

From the solution in sulphide of ammonium, the sulphides of arsenic and antimony are precipitated by an excess of dilute sulphuric acid, and separated and determined as in No. 61.

From the liquid which has been filtered off from the precipitate by sulphuretted hydrogen, the iron can only be separated by sulphide of ammonium after neutralizing with ammonia, on account of the presence of tartaric acid. When the sulphide of iron is completely separated by digestion at a gentle heat, it is filtered off, and washed with sulphuretted-hydrogen-water; the filter is then put into a beaker, and digested with hydrochloric acid until all the sulphide of iron is dissolved. The solution is then filtered off from the paper, the latter washed, the liquid heated with chlorate of potassa, and the sesquioxide of iron precipitated by ammonia.

Or the sulphide of iron is dried, removed from the filter, which is burned, and the ashes added to the precipitate, with a small piece of sulphur, and strongly ignited in a stream of dry hydrogen. It is weighed as Fe S—sulphide of iron.

If the amount of sulphide of iron be but small, the filter is ignited with the precipitate, the air having free access, until all the iron is converted into sesquioxide, and its weight remains constant.

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64. GERMAN SILVER (ARGENTAN).

(Cu, Ni, Zn).

The alloy is dissolved in nitric acid, the greater excess of acid evaporated, the solution diluted with water, and the copper precipitated by means of sulphuretted hydrogen. (*See* No. 30.)

The filtered liquor is concentrated by evaporation, precipitated by an excess of solution of potassa, and heated with it, when the protoxide of nickel is separated and the oxide of zinc dissolved. From this solution the latter is precipitated by sulphide of potassium, or, after being saturated with hydrochloric acid, by carbonate of soda at a boiling heat.

In this manner, however, the oxides of nickel and zinc cannot be separated with precision; some oxide of zinc remains with the protoxide of nickel.

The separation is also effected incompletely by fusing the mixture of the oxides with hydrated potassa, or by precipitating both oxides with carbonate of soda at a boiling heat, converting the protoxide of nickel into black sesquioxide by digestion with hypochlorite of soda, and then extracting the oxide of zinc by means of caustic potash, or the solution is mixed with acetate of soda and sulphuretted hydrogen passed into it. At first white sulphide of zinc is precipitated, and by degrees the black sulphide of nickel. A more accurate result is obtained if the mixture of both oxides is mixed with 3 times its weight of carbonate of potassa and the same quantity of sulphur, carefully fused together in a porcelain crucible, until it flows quietly, and when cool the alkaline sulphide extracted with water. Dilute hydrochloric acid is then poured upon the sulphides of the metals, which dissolves only the sulphide of zinc.

The most accurate method for the separation of the three metals consists in dissolving the German silver in hydrochloric acid, adding nitric acid, drop by drop, and saturating the solution, which must not be too acid, with sulphurous acid, and precipitating the copper as subsulpho-cyanide. (*See* No. 33.) The filtered solution is then evaporated to a small volume, mixed with an excess of caustic potassa, and gradually with hydrocyanic acid, until the precipitate is completely dissolved, and is of a yellow color. From this solution of double cyanides the zinc may be precipitated as a sulphide, by sulphide of potassium, and not sulphide of ammonium. After digestion by itself for some hours, at a gentle heat, it is filtered. The solution is then boiled with fuming nitric and hydrochloric acids, or in place of the latter, chlorate of potassa, and the protoxide of nickel precipitated while hot, by caustic potassa. It is then dried and ignited.

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65. NICCOLITE.*

Ni As.

I. PREPARATION OF PURE NICKEL.—The finely powdered arsenide of nickel is heated in a crucible placed obliquely in the fire where the draught is strong to carry off the fumes, and roasted at a gentle heat with continual stirring, until the vapors of arsenic cease to be given off, and it is changed into greenish basic arsenate of nickel.

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* Arsenide of nickel, with a varying amount of cobalt and iron. The smelting-products, known by the name of cobalt- and nickel-speiss, have a similar composition, and contain besides frequently accidental admixtures of copper and bismuth.

II. Or the powdered ore is mixed with 2 parts of dry soda, and 2 of saltpetre, in a clay crucible, and ignited for a considerable time. After the mass has cooled, all the arsenate of potassa is extracted by hot water, and the remaining oxide washed.

III. Or the ore is mixed with 2 parts of dry soda and 1½ parts of sulphur, in a clay crucible, and gradually heated to redness. It is kept at a low red heat for some time, being well covered. The sulph-arsenate and sulphide of sodium are extracted by water, after the mass has cooled, and the crystalline sulphide of nickel washed by decantation.

The mixture of oxides remaining behind in the first and second cases is dissolved in hot concentrated hydrochloric acid, that of the sulphides, in the third case, in hydrochloric acid with gradual addition of nitric acid and with application of heat.

The solution is heated to about 70°, and during that time, and until it has cooled, saturated with sulphuretted hydrogen; it is then allowed to stand in a closed vessel for twenty-four hours, when copper, bismuth, and a residue of arsenic are precipitated.

The arsenic is more easily precipitated if first converted into arsenious acid by heating with sulphurous acid. The solution must be freed from an excess of sulphurous acid by boiling, before the sulphuretted hydrogen is passed into it.

The sulphuretted hydrogen having been expelled by heat, the solution is filtered, heated to boiling, and precipitated by carbonate of soda; the precipitate, containing all the nickel, cobalt, and iron, is thoroughly washed.

It is then, whilst still moist, treated and digested with an excess of a hot saturated solution of oxalic acid, when all the iron is dissolved, and the nickel and cobalt are left in the form of oxalates. They are filtered off, washed, and digested with concentrated caustic ammonia until they are dissolved.

The blue solution is then set aside in an open vessel until all the free ammonia has evaporated (under a bell-jar over sulphuric acid, so that the ammonia may not all be lost), during which time the nickel separates in the form of green oxalate of protoxide of nickel and ammonia, whilst the cobalt remains in the solution to which it imparts a red color.

The nickel-salt is filtered off, washed, and ignited in a closed crucible or in a glass tube, when pure metallic nickel remains behind.

The cobalt may be obtained from the solution by evaporation and ignition of the residue, or by boiling it with caustic potassa until no farther disengagement of ammonia takes place; or when smaller quantities are operated upon, by an alkaline sulphide, and subsequent addition of dilute sulphuric acid in order to separate the sulphide of cobalt. It however still contains nickel.

The pure metal may be easily prepared from commercial nickel by dissolving it in hydrochloric acid with the addition of some nitric acid, purifying the solution by sulphuretted hydrogen, and then precipitating nickel and cobalt by the addition of a boiling saturated solution of binoxalate of potassa. The washed precipitate is then ignited, the metal dissolved in hydrochloric with nitric acid and cobalt and nickel separated by nitrite of potassa.

For the purpose of separating the iron, the solution, after being again oxidized, may also be mixed with chloride of ammonium, and then with ammonia in excess, when sesquioxide of iron (with a little nickel and cobalt) is precipitated, whilst nickel and cobalt remain in solution.

II. Quantitative Analysis.—The very finely-powdered arsenide of nickel is fused with 2 parts of nitrate of potassa and 2 parts of carbonate of soda, in a platinum crucible, the bottom and sides of which have previously been carefully covered with carbonate of soda; the mass is then ignited for some time, and when cold is digested with water; the oxides formed are filtered off and thoroughly washed.

The solution contains all the arsenic in the form of arsenates of the alkalies; it is supersaturated with hydrochloric acid, and then mixed with concentrated caustic ammonia and sulphate of magnesia.

After twenty-four hours the precipitate is collected on a weighed filter, washed with dilute caustic ammonia, dried at 100° and weighed. (*See* No. 51.)

The arsenic may also be determined from the loss.

The oxides are dissolved in concentrated hydrochloric acid, and the copper and bismuth precipitated from the solution by sulphuretted hydrogen. The precipitate is treated as in No. 50.

The liquid filtered off from the precipitate is heated nearly to boiling, and mixed with some chlorate of potassa in order to peroxidize the iron, which may then be separated from the nickel and cobalt in the same manner as from manganese, either by succinate of ammonia or by carbonate of baryta. (*See* No. 25.)

From the liquid filtered off from the succinate of iron, nickel and cobalt are precipitated at a boiling-heat by caustic potassa, filtered off, and washed with hot water.

From the liquid separated from the carbonate of baryta, the dissolved baryta is precipitated by sulphuric acid, and the nickel and cobalt are then precipitated from the hot solution by caustic potassa.

The precipitate containing the hydrated oxides of nickel and cobalt is gradually mixed, whilst still moist, with dilute hydrocyanic acid and solution of potassa (or cyanide of potassium), and a gentle heat applied until it is dissolved. The yellowish-red solution is heated to boiling, in order to expel the excess of the hydrocyanic acid and to convert the cyanide of cobalt and potassium into the cobalticyanide, and is then mixed, whilst still warm, with levigated protoxide of mercury. By this treatment the cyanide of nickel and potassium is decomposed and all the nickel precipitated, partly in the form of oxide, partly as cyanide, whilst mercury takes its place.

The precipitate, when washed and ignited with access of air, leaves pure oxide of nickel behind.

If the mixture of both oxides, previously to the treatment with hydrocyanic acid and potassa, have been dried and reduced to metal by igniting it in a current of hydrogen (and the metal weighed), the amount of cobalt need not now be determined directly.

If this be not the case, the solution which still contains the cobalt is carefully neutralized with nitric acid, and solution of nitrate of suboxide of mercury, as neutral as possible, added, as long as it produces a white precipitate of cobalticyanide of mercury. After being washed and dried, the precipitate is ignited with access of air, when it is converted into black oxide of cobalt, which, after being weighed, must be reduced by strong ignition in a current of hydrogen, on account of its amount of oxygen varying according to the temperature.

When the nickel-speiss contains lead and sulphur, the same method is used which has been given for the analysis of tetrahedrite, where the compound is decomposed by heating it in a current of dry chlorine gas.

Another good method of separation of nickel from cobalt is the following: the solution of both oxides is made as concentrated as possible, and neutralized with potassa, mixed with a concentrated solution of nitrite of potassa, acidified with acetic acid and allowed to stand for twenty-four hours. The yellow precipitate of nitrite of sesquioxide of cobalt and potassa (Co_2O_3,

$3 KO, 5 NO_3 HO$) is filtered, washed with a solution of chloride of potassium, dissolved in hydrochloric acid and the protoxide of cobalt precipitated by caustic potassa. Protoxide of nickel may be precipitated from the filtered solution in the same manner.

If nickel is to be precipitated from a solution by means of sulphide of ammonium, it is not complete, leaving sulphide of nickel undissolved, giving a brown color, if the sulphide of ammonium does not contain, by means of oxidation, a higher sulphide.

The best method is to saturate the nickel solution with sulphuretted hydrogen, and drive off so much ammonia that the solution is feebly alkaline. Then filter as quickly as possible, and wash the precipitate with water containing sulphuretted hydrogen.

66. SMALTITE.

Speiss Cobalt.*

$(Co, Fe, Ni) As_2$.

The analysis and the preparation of pure cobalt can be effected by the same process as the analysis of copper-nickel and the preparation of pure nickel.

Since the arsenide of cobalt contains upwards of 70 per cent. of arsenic, it is advisable to remove a great portion by first fusing it with common salt, and afterwards roasting or fusing it with a mixture of soda and sulphur.

It may be separated from nickel by nitrite of potassa. For the preparation of fused metallic cobalt, the yellow precipitate is dissolved in the smallest possible quantity of hydrochloric acid, the solution mixed with acetate of soda, and the pale rose-red oxide of cobalt precipitated by a hot saturated solution of oxalic acid. The yellow salt may also be changed directly to an oxalate by boiling with oxalic acid. After it is washed and dried, it is placed in an unglazed porcelain crucible, standing in a Hessian crucible, pressed in firmly, both crucibles covered and luted, and then placed in a strong blast or furnace fire.

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* Arsenide of cobalt, with small quantities of nickel, iron, and copper.

The cobalt may also be separated from the nickel, if the solution mixed with hydrochloric acid is considerably concentrated by evaporation, mixed with sal-ammoniac and ammonia in excess, and the brown solution allowed to stand exposed to the air until it has acquired a fine purple tint. If it be now saturated with hydrochloric acid and heated to boiling, the greater portion of the cobalt separates in the form of a carmine crystalline powder, which appears to be $5NH_3+Co_2Cl_3$, and when ignited leaves protochloride of cobalt.

If dissolved in boiling dilute hydrochloric acid, this compound crystallizes in dark red octahedral crystals. Heated alone blue chloride of cobalt is formed, in hydrogen gas, metallic cobalt.

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67. COBALTITE.

CoS_2+CoAs_2.

I. The finely-powered mineral is decomposed by heating it in a current of dry chlorine-gas, as in the analysis of tetrahedrite, when the cobalt remains behind in the form of protochloride, whilst arsenic and sulphur are obtained as acids, dissolved in the water of the receiver. The protochloride of cobalt can then immediately be reduced to metal, in the same tube, by heating it in hydrogen, and weighed, if the determination of the small amount of iron contained in it be neglected; or it is dissolved in water acidulated with hydrochloric acid, and the solution precipitated at a boiling heat by caustic potassa. The small amounts of nickel and iron contained in the oxide of cobalt are then determined as in No. 66.

The sulphuric acid is determined by means of chloride of barium, and the excess of baryta removed by sulphuric acid. The filtered solution is concentrated by evaporation, and the arsenic acid precipitated by sulphate of magnesia and ammonia as in No. 65.

II. The mineral is dissolved in concentrated hydrochloric acid, with gradual addition of nitric acid, until it is completely dissolved, or the undissolved sulphur is left behind with a fine yellow tint. The latter is then collected on a weighed filter, dried at 100° and weighed.

From the solution the sulphuric acid is precipitated by chloride of barium, and the amount of sulphur calculated from the precipitate, is added to that directly determined.

The excess of baryta is removed from the solution by sulphuric acid.

The filtrate is mixed with sulphurous acid, allowed to stand for twenty-four hours, then heated to boiling until the excess of sulphurous acid is completely driven off, and when cooled down to about 50°, saturated with sulphuretted hydrogen. Thus saturated, it is left to stand for twenty-four hours, the sulphuretted hydrogen removed by gentle evaporation, and the sulphide of arsenic collected on a weighed filter and dried at 100°. It is then treated as in No. 52.

The solution of cobalt filtered from this precipitate is heated to boiling, mixed with a little chlorate of potassa, in order to bring the iron to a higher state of oxidation, carefully neutralized with carbonate of soda, acetate of soda added and heated to boiling, which precipitates the iron free from cobalt.*

The protoxide of cobalt is precipitated from the filtered solution at a boiling heat by means of caustic soda, washed with hot water, ignited, and reduced in a current of hydrogen at as high a temperature as possible. When moistened with water after being weighed, the metal must not exhibit an alkaline reaction. Any nickel present may be determined as in No. 65.

III. The mineral is fused with carbonate of soda and saltpetre as in the analysis of copper-nickel, No. 65. The mass is then treated with warm water, and the black oxide of cobalt filtered off. The solution is slightly acidified with hydrochloric acid and the sulphuric acid precipitated by chloride of barium. After the excess of baryta has been removed by sulphuric acid, the solution is concentrated by evaporation, mixed with sal-ammoniac and sulphate of magnesia, and the arsenic acid precipitated by ammonia.

The oxide of cobalt is dried, the filter incinerated, the ash added to the oxide, and the whole dissolved in concentrated hydrochloric acid. The sesquioxide of iron is then precipitated, by means of succinate of soda, from the dilute solution, after carefully neutralizing with carbonate of soda, and the cobalt and nickel separated as above.

The sesquioxide of iron cannot be precipitated, in this case, by carbonate of baryta, because some oxide of cobalt is precipitated at the same time; neither does the precipitation by an excess of ammonia lead to exact results, on account of some oxide of cobalt remaining combined with the sesquioxide of iron.

An approximate separation of both oxides may also be effected by neutralizing the solution with ammonia, precipitating both metals by sulphide of ammonium, and then adding a slight excess of dilute hydrochloric acid, when sulphide of iron is dissolved and sulphide of cobalt is left undissolved.

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* From a solution of nickel, iron thus precipitated always contains some of the nickel.

Or both oxides are precipitated by caustic potassa, the precipitate washed, removed from the filter, and the latter carefully cleansed with water from the washing-bottle; the mass is then mixed with a slight excess of powdered oxalic acid, when the oxide of cobalt is converted into rose-colored, insoluble oxalate, whilst the sesquioxide of iron is dissolved. After twenty-four hours the former is collected on a weighed filter, washed with cold water, dried at 100°, and a weighed portion of it ignited in a glass tube, one end of which is sealed, whilst the other is drawn out into a point; by this process the oxalate of cobalt is reduced to metal. Whilst the tube is still red-hot the point is sealed with the blow-pipe, and the tube weighed when cold.

68. MANGANESE AND COBALT, OR NICKEL.*

For the merely approximate separation, the oxides are precipitated by carbonate of soda, the precipitate dissolved in an excess of acetic acid and the cobalt or nickel precipitated from the solution by sulphuretted hydrogen, when manganese remains dissolved. The solution of the chlorides or of the sulphates may also be mixed with acetate of soda, and the nickel or cobalt precipitated by sulphuretted hydrogen.

Or the solution is mixed with considerable chloride of ammonium, saturated with ammonia, and the manganese precipitated by phosphate of soda. After ignition the precipitate consists of $2MnO, PO_5$.

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* **Black cobalt-ore (earthy ore of cobalt) is a compound of protoxide of cobalt with binoxide of manganese. Moreover, almost every variety of manganese-ore contains small quantities of cobalt for the detection of which the residues of the preparation of chlorine may be used.**

A more accurate, but still not absolute separation, may be effected by neutralizing the solution of the chlorides with ammonia, precipitating the metals by sulphide of ammonium, and mixing the solution with an excess of very dilute hydrochloric acid, when the sulphide of manganese is dissolved with great facility, whilst the sulphides of nickel or cobalt remain undissolved.

This method of separation is perfectly exact if the sulphides be used which were formed at a high temperature. The oxides are precipitated at a boiling heat by carbonate or hydrate of soda, the precipitate ignited and weighed, and then heated to dull redness in a current of sulphuretted hydrogen, in a porcelain boat, placed in a porcelain tube. When cold, the porcelain boat is put into very dilute hydrochloric acid, which dissolves the manganese only, and leaves the sulphide of cobalt or nickel behind. The conversion of the oxides into sulphides may likewise be effected by fusing them in a porcelain crucible with 3 times their weight of carbonate of soda and as much sulphur, after which the mass is treated with dilute hydrochloric acid.

Or nitrite of potassa is added to the concentrated solution of the three metals, which precipitates the cobalt as in No. 65. Acetate of soda is added to the filtered solution, and chlorine gas passed into it, when all the manganese is precipitated as superoxide. The nickel and iron remain in solution, but the cobalt is precipitated with the manganese.

69. METEORIC IRON.

Iron of meteoric origin can be recognized by the following peculiarities:—

I. Some meteoric iron contains olivine, which may be detected by the eye, also gold-colored sulphuret of iron.

II. In certain kinds, especially on the oxidized surface, yellowish, pliable laminæ of a metallic lustre may be observed; they are phosphide of nickel and iron (Schreibersite).

III. Some kinds are passive, *i. e.*, they do not reduce copper from a solution of neutral sulphate of copper.

IV. If a freshly filed, ground and polished surface be immersed for five or ten minutes in dilute nitric acid, peculiar, mostly crystalline delineations (Widmannstätten's figures), or microscopic parallel lines or bright points, make their appearance in most kinds, thus imparting to the surface a peculiar lustre when viewed in a certain direction.

V. All meteoric iron, when dissolved in hydrochloric acid, leaves a black, pulverulent residue, whilst in most cases a trace of sulphuretted hydrogen is developed, derived from an admixture of sulphide of iron. On examining this residue (previously washed and dried) under a magnifying power of from 50 to 100, in most cases crystalline particles of metallic lustre, and frequently also well-defined magnetic prisms of metallic lustre, are observed, consisting of phosphide of iron, phosphide of iron and nickel, and sometimes also chrome-iron and graphite; in addition to these also transparent, partly colorless, partly colored grains of quartz, olivine and other minerals.

VI. Every specimen of iron of undoubted meteoric origin contains as characteristic constituents, nickel, cobalt and phosphide of iron and nickel. The amount of nickel varies between 2 and 20 per cent.; the cobalt rarely amounts to 1 per cent., and the insoluble residue usually amounts to 3 per cent.

In order to detect the nickel, the hydrochloric solution is first saturated with sulphuretted hydrogen in order to precipitate traces of copper and tin, which occasionally occur; the protochloride of iron is then converted into sesquichloride by heating the solution nearly to boiling, and adding small quantities of chlorate of potassa. The solution is then mixed with an excess of ammonia, when all the sesquioxide of iron is precipitated, whilst most of the nickel remains dissolved. When the amount of nickel is rather large, the filtered liquor is more or less blue. Sulphide of ammonium precipitates from it black sulphide of nickel.

Or the solution is neutralized with carbonate of soda, acetate of soda added and boiled, when the iron with only a trace of nickel is precipitated, the nickel and cobalt remain in solution.

In order to detect the phosphoric acid contained in the sesquioxide of iron, it is dried and ignited with an equal weight of carbonate of potassa and soda, and the alkaline phosphates extracted with water. The solution is then supersaturated with acid and the phosphoric acid precipitated by ammonia and sulphate of magnesia.

In order to obtain the amount of phosphorus contained in the black residue left on dissolving meteoric iron in hydrochloric acid, it is finely powdered, mixed with about half its weight of nitrate of potassa and then with an equal weight of carbonate of soda, and ignited; the mass is then extracted with water and treated as above. The oxidized residue is dissolved in hydrochloric acid and the nickel detected as above.

In quantitative analyses the iron is separated from the nickel and cobalt, either by succinate of ammonia, or by carbonate of baryta, *see* No. 25. The phosphoric acid is contained in both precipitates. Cobalt and nickel are separated by cyanide of potassium as in No. 65.

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70. THE PLATINUM METALS AND ORE.

1. Platinum.—Only fusible in the oxyhydrogen flame. Density when fused is 21.15. Free from iridium it is very soft and malleable. Soluble in aqua regia. The reddish-yellow solution gives with the salts of ammonium and potassium a crystalline lemon yellow precipitate, $NH_4 Cl + Pt Cl_2$ and $K Cl + Pt Cl_2$. The former ignited forms a gray platinum sponge, and the latter, fused with common salt, crystallized platinum.

2. Palladium.—In color, lustre, and malleability, similar to platinum. Difficultly fusible, but more easily than platinum. Density 11.8. Heated in the air it is colored steel-gray, and in the flame of a gas burner becomes rusty, and uniting with carbon becomes brittle. Soluble in cold nitric acid without disengagement of gas. Its oxides are Pd_2O, PdO, and PdO_2; they are black and reduced without a flux.

In aqua regia it gives a dark-brown solution of perchloride. By evaporation it becomes a dark-brown deliquescent protochloride $Pd Cl$. Iodide of potassium added to this solution forms a black iodide of palladium, PdI, and cyanide of mercury a yellowish-white cyanide of palladium $Pd Cy$.

Ammonia throws down a flesh-red crystalline precipitate $Pd Cl + NH_3$, forming a colorless solution if an excess of ammonia is added. Hydrochloric acid gives in this solution a lemon-yellow crystalline precipitate $= N. PdH_3 + Cl$, which leaves, after ignition, the gray metal. If one and a half times the weight of the metal of chloride of potassium be added to the solution of palladium in aqua regia, and evaporated to dryness, a dark red crystalline $Pd Cl_2 + K Cl$ is formed, insoluble in alcohol, scarcely soluble in water, a means by which the commercial palladium, iron, and copper may be separated.

3. IRIDIUM.—More fusible than platinum. Specific gravity = 21.15. In its isolated form it is unacted on by any of the acids, or by aqua regia, unless alloyed with platinum. To obtain the metal in the separate state the powdered alloy is intimately mixed with an equal weight of finely powdered chloride of sodium, and the mixture heated to dull redness in a glass tube through which a current of dry chlorine is passed so long as it is absorbed. The resulting dark-red solution of double chlorides gives, with chlorides of ammonium and potassium in a hot solution, a black precipitate of $NH_4\,Cl + Ir\,Cl_2$, or $KCl + Ir\,Cl_2$.

If the metal is fused with nitrate of potassa at a strong red heat, or with caustic potassa and chlorate of potassa, it is converted into a black sesquioxide, mixed with potassa. The pulverized metal heated to redness oxidizes in the air.

4. RHODIUM.—More infusible than platinum. After fusion it has a specific gravity 12.1. Malleable. If heated to redness in the form of a powder in the air, it oxidizes. Insoluble in aqua regia. It is obtained as a soluble double salt if gently ignited in a stream of chlorine, if pulverized and mixed with chloride of potassium, or chloride of sodium. Both double salts ($2KCl + R_2\,Cl_3$) are easily soluble in water, also the ammonium salt. They are insoluble in alcohol. They form dark-red crystals. Potassa added to their solutions, and then alcohol, a black precipitate of rhodium is formed. The pulverized metal fused for some time with a large excess of bisulphate of potassa, and until the free acid is driven off, forms a mass soluble in water. If chloride of potassium and hydrochloric acid are added to this solution and evaporated, it becomes rose-red.

5. RUTHENIUM.—Still more infusible than the preceding metals. Sp. gr. = 11.3. Brittle. Pulverized and heated in the air it is oxidized, fused with hydrate of potassa and saltpetre or chlorate of potassa, it forms ruthenite of potassa, $KO, Ru O_3$, forming with water a yellow solution. Neutralize this solution with nitric acid, and a black sesquioxide is thrown down, which is easily reduced in hydrogen gas. The double chloride of ruthenium and potassium, $K Cl + Ru Cl_2$ is easily soluble in water, but insoluble in alcohol. The red solution is not precipitated by potassa and alcohol in the cold. If a stream of chlorine gas is conducted into a solution of ruthenite of potassa ruthenic acid is obtained, which is very volatile, of a yellow color, with a strong odor, difficultly soluble in water, and soon changing to black.

6. OSMIUM.—This metal alone is infusible in the strongest oxyhydrogen flame, but forms a bluish metallic mass with sp. gr. = 21.4 It volatilizes at the highest temperature. It is obtained with all these properties, if sulphide of osmium is heated in a strong coke fire, in a close covered graphite crucible. It may be prepared in the crystalline form by fusing the pulverized osmium with six or eight times its weight of tin in a graphite crucible, slowly cooled, and the tin dissolved by hydrochloric acid. Or it is obtained as a bluish-black powder mass, when chloride of ammonium is added to a solution of osmiate of potassa or ammonia, evaporated to dryness, and the mass heated in a porcelain retort until the chloride of ammonium begins to volatilize; heating this with water, the osmium remains.

The smallest quantity of osmium on platinum foil, held in the flame of a spirit lamp, becomes brilliant, and imparts the characteristic odor of osmic acid. Osmium, heated in a slow stream of oxygen, forms osmic acid. It is also formed by oxidizing with nitric acid. It is very volatile, condenses in colorless crystals, soluble in water, with a very pungent odor extremely irritating and deleterious to the eyes and organs of respiration. If passed in the vapor form with hydrogen through a glass tube heated to redness, it is reduced to a mirror of metallic osmium. The solution heated with sulphurous acid becomes violet. Potassa precipitates a black oxide containing potassa, and easily reduced by hydrogen. The solution becomes yellow with potassa and ammonia. The osmiate of potassa is deep yellow crystalline. Its solution mixed with alcohol precipitates dark red crystalline osmite of potassa $KO, Os\,O_2$. If chloride of ammonium is added to this last solution, a pale yellow crystalline salt of ammonium and osmium is precipitated, which, after it is ignited in a current of hydrogen, leaves metallic osmium.

Both the chlorides of osmium are volatile. The protochloride, $Os\,Cl$, is green, the bichloride, $Os\,Cl_2$, is dark red. The double chloride, $K\,Cl + Os\,Cl_2$, forms dark-brown octahedrons, giving a yellow solution in water.

PLATINUM ORE.

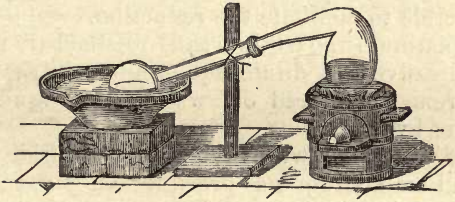
(Platinum with small quantities of Iridium, Palladium, Rhodium, Osmium, Ruthenium, Iron and Copper.)

The commercial platinum ore usually contains grains of sand, of osmium, iridium, and often of gold. In order to find the latter the mass is digested in rather dilute aqua-regia, until scales of gold are no longer visible. The solution is then poured off from the undissolved platinum, freed from nitric acid by evaporation, diluted, oxalic acid added, and the gold precipitated by means of heat. It is washed, ignited, and weighed.

The sand is determined in the following manner: A small quantity of borax is fused in a clay crucible, so that the sides may be covered with it, then eight grains of finely-divided silver are placed in it, and upon this two grains of platinum ore, which is covered with about ten grains of fused borax. The mixture is kept in a state of fusion for some time at a temperature sufficient to melt the silver. After cooling the regulus is freed from slag and weighed. All the sand is taken up by the slag and the metal by the silver.

For analysis, ten grammes of the grains of real platinum are picked out and dissolved at a boiling heat, in a mixture of five parts of fuming hydrochloric acid and one part of fuming nitric acid, in a retort connected with a receiver which is to be kept perfectly cold.

Fig. 14.



The acid is distilled off until the contents of the retort have acquired the consistence of a syrup. The mass becomes solid on cooling; it is then dissolved in a small quantity of water and the clear solution carefully poured off from the residue. The acid which was distilled over contains osmic acid, and is colored yellow by a portion of the solution which was mechanically carried over; it is poured back on the residue and again distilled, in order to complete the solution.

The distillate containing osmic acid may be saturated with ammonia and the osmium separated as in No. 71. Or it is nearly saturated with hydrate of lime, mixed with an alkaline formate and boiled, when the osmium is reduced as a bluish-black powder, which is ignited in a current of hydrogen when the osmium is obtained in the metallic state, and weighed.

The platinum-solution is filtered off from the insoluble residue, which is collected on a weighed filter and washed. It consists of irid-osmine, and is farther treated as in No. 71.

The solution is evaporated to dryness, the mass heated to 150° in order to convert the chloride of iridium into sesquichloride. It is then dissolved in a little water containing a few drops of hydrochloric acid, mixed with a concentrated solution of chloride of ammonium, the precipitate filtered off, washed with a solution of chloride of ammonium, and then with alcohol. The double salt, when dried, is ignited with the filter, a few crystals of oxalic acid being placed in the crucible to facilitate the reduction.

The platinum and iridium thus obtained are weighed, again dissolved in dilute aqua-regia, and the iridium which remains filtered off, washed, and ignited in a stream of hydrogen.

The filtrate from which the double chloride of platinum and ammonium was precipitated, is concentrated by evaporation, boiled with concentrated nitric acid to decompose the chloride of ammonium, saturated with chlorine gas until the solution of chloride of iridium has a brownish-red color. It is then completely evaporated to dryness on a water-bath, the mass pulverized and treated with alcohol of 80 per cent., filtered and washed with alcohol until it flows through colorless. This solution contains all the iron and copper which are determined by themselves.

The insoluble salt, which contains besides the osmium and ruthenium, all the platinum metals, is washed with a weak solution of chloride of ammonium until the reddish solution becomes colorless. This solution contains all the rhodium and palladium. It is evaporated to dryness, ignited in a covered platinum crucible, and the metal reduced in a current of hydrogen. The weighed metal is digested with dilute aqua-regia, the solution which contains all the palladium with a little rhodium, evaporated to dryness, a few drops of caustic potassa added, and the palladium precipitated by a saturated solution of cyanide of mercury. The precipitate is washed, dried, ignited in a stream of hydrogen, and weighed as metallic palladium.

The solution which contains the rhodium, is made slightly alkaline with soda, evaporated to dryness, the mass ignited to drive off the mercury and treated with water. The oxide of rhodium which remains undissolved is added to that left from the solution of the palladium and ignited in hydrogen gas.

The portion of the salt which contained the platinum and iridium, and which remained insoluble in the chloride of ammonium, is digested with a weak solution of cyanide of potassium added gradually, until the color has changed to a light yellowish-brown, and is converted into a double salt of chloroplatinate of potassium and ammonium, which is washed with a solution of chloride of ammonium. By dissolving in boiling water it is obtained in dark yellow octahedral crystals. It is ignited, placing in the crucible near the close of the operation some crystals of oxalic acid, and the chloride of potassium extracted with water.

The filtrate which contains the iridium is evaporated to dryness, ignited to drive off the chloride of ammonium, and finally fused with some nitrate of potassa. The sesquioxide of iridium containing the alkali which remained insoluble when treated with water, is well washed, reduced by hydrogen, and the alkali extracted with water.

71. IRIDOSMINE AND PLATINUM RESIDUES.

I. Iridosmine occurs in small scales and mostly steel colored, extremely hard, and of sp. gr. 18 to 20. It is contained entirely in the residue in the solution of platinum, mostly in the form of very fine plates. Its composition is variable. Besides the two principal metals, it contains more or less rhodium and ruthenium, with small quantities of platinum, copper, and iron. It is insoluble in aqua regia.

The osmium may be extracted for the most part from the variety made up of very fine grains* or powder by roasting. The ore is placed in a porcelain tube heated to redness, and a slow stream of air or oxygen gas passed over it. The end of the porcelain tube passes into a well-cooled receiver, from which the osmic acid is conducted into a solution of caustic potassa.

The fine pulverulent variety is mixed with an equal weight of common salt, and a stream of moist chlorine passed over it, in a porcelain tube heated to redness, and then treated as in No. 71, II.

In order to pulverize the coarse grained kind, it is fused with six times its weight of pure zinc, in a crucible placed in a second crucible and surrounded by charcoal powder, well covered and heated to redness for half an hour and to a white heat for two hours until all the zinc is volatilized. The iridosmine is left in the form of a glistening friable sponge.

From this sponge the osmium may be volatilized by heating in the oxyhydrogen flame, the iridium containing ruthenium and rhodium will be fused.

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* A species in form of a very heavy gray salt, and probably obtained from the dressing of the gold sands of California, contains still more gold and much chloride of silver, which must be extracted by concentrated ammonia before it is made use of.

Species containing sand must be purified by fusing with carbonate of soda and treating the mass with water.

The pulverulent iridosmine is easily separated by fusing in a silver crucible with caustic potassa and chlorate of potassa. It is heated carefully in the beginning on account of the frothing, but finally to redness. The mass is treated with water, until dissolved, and then left in a high closed vessel until it has settled clear. The deep yellow solution of osmiate and rutheniate of potassa are drawn off clear by means of a syphon, and the black residue, consisting of oxides of rhodium and iridium treated again in the same manner with water. From the yellow solution ruthenium is precipitated as a black oxide by carefully neutralizing with nitric acid. It is reduced by means of hydrogen.

The solution containing osmium is made alkaline with potassa, alcohol added and heated, whereby the osmium is precipitated as a black oxide containing potassa. It is ignited in hydrogen and the potassa removed by water.

The oxide of iridium is reduced by heating in hydrogen, washed, intimately mixed with an equal weight of fused chloride of sodium, and gently ignited in a current of chlorine, until the gas passes off unabsorbed in excess. The resulting double chloride is dissolved in water, the solution concentrated and mixed with an excess of a hot saturated solution of chloride of potassium, when the iridium is precipitated as a black crystalline double chloride. It is then washed with a saturated solution of chloride of potassium. (It may also contain some of the ruthenium salt precipitated at the same time. In order to extract this the metal is fused with caustic and chlorate of potassa.)

The solution which contains the rhodium and the ruthenium is concentrated, formate of soda added and boiled, when all the rhodium is precipitated. The filtrate is acidified with hydrochloric acid, and the ruthenium precipitated by pure zinc.

The following method may be used for the analysis of iridosmine. Two grains of the substance, in a fine powder, are intimately mixed with six grains of peroxide of barium and two of nitrate of baryta* in a close covered silver crucible, and heated to redness for about two hours. The unfused mass is taken from the crucible, treated with water, and hydrochloric acid added until it dissolves. It is then mixed with nitric acid, and gently boiled until the smell of osmic acid is no longer perceptible.† It is then carefully evaporated to dryness, dissolved in hot water, the liquid decanted from the iridosmine, which has been somewhat acted upon.

The baryta in the solution is precipitated by sulphuric acid, and after it has completely settled, and the liquid become clear, it is filtered.

About eight grammes of pure chloride of ammonium are mixed with the yellowish-red solution, evaporated to dryness, and a small quantity of chloride of ammonium mixed with alcohol added to the mass, the salt of iridium filtered off, washed as at first, with a solution of chloride of ammonium, then with weak and afterwards strong alcohol. The dried salt, together with the filter, is placed in a covered platinum crucible and very gradually and carefully heated to redness, the filter then thoroughly burned, and the metal reduced by conducting hydrogen gas into the crucible or holding a piece of carbonate of ammonia in it while heated.

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[*] These two products should be very accurately weighed, in order to determine beforehand the exact quantity of sulphurous acid necessary to precipitate the baryta. The nitrate of baryta must be decrepitated.

[†] The osmic acid may be driven off in a retort and absorbed by a solution of ammonia.

The ruthenium is combined with the iridium. They are separated, as already stated, by fusing with caustic and chlorate of potassa.

The rhodium is contained in the remaining solution of chloride of ammonium. It is heated with a large excess of nitric acid, evaporated to a small quantity, placed in a weighed porcelain crucible, evaporated to dryness, and the salt, heated to redness, is reduced by conducting a stream of hydrogen upon it.

The iron, copper, baryta, and alumina (the last from the peroxide of barium) are separated by alternate treatment with hydrochloric and nitric acids.

The solution is neutralized with carbonate of soda, and the palladium precipitated by a solution of cyanide of mercury. The yellowish-white cyanide of palladium having settled, it is filtered off, washed, and ignited, when metallic palladium is left behind.

The filtered solution is boiled with hydrochloric acid until it has assumed a red tint, and the hydrated oxide of rhodium is then precipitated by caustic potassa. By ignition in hydrogen it is reduced to the metallic state.

From the solution which contains the rhodium and palladium both metals may also be precipitated by pure zinc, with the addition of hydrochloric acid, the precipitate washed, and the palladium extracted by nitric acid, in which the rhodium is insoluble.

If the rhodium be not reduced by formic acid, the solution obtained with bisulphate of potassa might also be mixed with formate of soda and boiled, when palladium is separated in the metallic state. If both be reduced, the palladium could be extracted from the mixture by means of nitric acid.

II. PLATINUM-RESIDUES.

There are two kinds. The kind A is that which remains insoluble when large quantities of platinum ore are dissolved; the kind B is obtained as a precipitate by iron in the last mother liquor from the preparation of platinum.

A. This residue is formed of grains and scales of irid-osmine, together with pulverulent iridium with very small quantities of palladium, rhodium, and platinum, mixed with titanic iron, chromic iron, and sand. These last three sometimes amount to 70 or 80 per cent., and also contain traces of chlorides of silver and gold. To extract the precious metals a variety of methods are employed.

The coarse granular kind is broken and ground as finely as possible, to reduce the grains of the iron ores to powder. It is then levigated with water, when most of the irid-osmine is separated in larger grains and scales.

1. The levigated black powder is intimately mixed with about its own bulk of decrepitated and finely-powdered chloride of sodium, the mixture introduced into a porcelain or glass tube, and gently ignited in a slow current of undried chlorine-gas until the latter commences to pass through the tube unabsorbed.

The other end of the tube dips into a well-cooled, tubulated receiver from the tubulure of which a gas-tube conducts the excess of chlorine into milk of lime.

By this process sodio-chlorides of iridium and of osmium are formed. The greater portion of the latter is decomposed by the moisture of the chlorine-gas, and the osmic acid formed from it partly sublimes in the receiver, and is partly conducted into the hydrate of lime.

The residue in the tube, when cold, is treated with water, and is at last washed with hot water.

The dark yellowish-red solution of iridium filtered off from the iron ore is mixed with concentrated nitric acid and distilled, when osmic acid passes over, dissolved in water. The liquid thus very much concentrated, is, whilst still hot, mixed with a saturated solution of chloride of potassium, when, on cooling, a great portion of the iridium separates in the form of crystalline black chloride of iridium and potassium, which is filtered off and several times washed with solution of chloride of potassium.

The remaining solution is mixed with crystallized carbonate of soda in excess, evaporated to dryness, the mass gently ignited in a crucible, and when cold washed with hot water, which usually acquires a yellow color, owing to the presence of an alkaline chromate.

The black powder which is left undissolved, consists of a compound of sesquioxide of iridium with soda, contaminated with sesquioxide of iron. It is reduced by being gently heated in a current of hydrogen. Water then extracts caustic soda, and the iron is removed by digestion with hydrochloric acid. On digesting it, after this treatment, with some very dilute nitro-hydrochloric acid, a small amount of platinum is usually extracted, which may then be precipitated with chloride of ammonium.

The iridium in the first solution may be precipitated by chloride of ammonium instead of chloride of potassium. When the black perchloride of iridium and ammonium is washed with a solution of chloride of ammonium, and then digested with a solution of cyanide of potassium, it is completely dissolved if it is free from platinum, as a protochloride. If it contains platinum, there remains undissolved a light brown residue, soluble in hot water, which crystallizes in dark yellow octahedrons. This salt has the composition expressed by the formula $(NH_4, K)\,Cl + Pt\,Cl_2$.

Or the chloride of iridium and ammonium or potassium is melted in a porcelain crucible with one and a half times its weight of cyanide of potassium, the mass dissolved in a little water, filtered, an excess of acetic acid added to decompose the free cyanide of potassium, heated to boiling (whereby red sesqui-cyanide of rhodium may be precipitated), and the platinum precipitated by sulphate of copper. The violet precipitate, a mixture of double cyanide of platinum and copper, and of double cyanide of iridium and copper, is washed with hot water and then boiled with caustic baryta. The cyanides of platinum and of barium, very soluble in hot water, but scarcely soluble in cold, may be easily separated from the colorless and more soluble salts of iridium by crystallization.

The iridium reduced by hydrogen and freed from iron, may contain ruthenium and rhodium. To extract the first it is fused with caustic potassa and chlorate of potassa, and afterwards to extract the latter with bisulphate of potassa. (*See* No. 70.)

The sesquioxide of iridium from the metal obtained by the calcination of the double chloride of ammonium, may be brought to a coherent mass by a strong pressure, and heating to a white heat; it is then placed in a burnt lime crucible, and fused by an oxyhydrogen jet.

The metal may be extracted from the osmic acid by the process given in No. 70.

A single treatment of a platinum residue is not generally sufficient, but it must be repeated several times.

2. The minerals mixed with the platinum metals are separated by fusing the residues with a flux, and lead, which dissolves the noble metals. The platinum residue is mixed with (not more than 300 or 400 grms. at a time) an equal weight of granulated lead, and one and a half times its weight of litharge, and melted in a crucible with a thick bottom, until completely fused. It is stirred from time to time with an earthenware rod to unite the grains of metal, the crucible is taken from the fire (before the oxide of lead has penetrated it), gently struck a few times and left

to cool. The lead button formed is freed from slag, and dissolved in moderately strong hot nitric acid. The platinum metals remain in the state of a black powder, and as grains and scales. They are then treated as above.

In the lead solution which may contain palladium, the lead is precipitated by sulphuric acid. It is then evaporated to dryness, the mass again dissolved in a little water, and the palladium precipitated by cyanide of mercury.

Another good flux for this operation, which attacks the crucible less, is a mixture of fluorspar and anhydrous gypsum of equal equivalent weights (1 pt. CaF, and 1.7 pt. CaO, So_3), 1 pt. of platinum residue, 1 pt. granulated lead, and 2 pts. of flux.

3. The platinum residue is fused with an equal weight of caustic potassa and twice its weight of nitrate of potassa, in an iron crucible, finally heated to redness with frequent stirring. The mass is poured out, coarsely powdered, hot water added, mixed with one-tenth alcohol, and boiled until completely decomposed. By this means the osmate of potassa is changed to osmite, the ruthenite of potassa completely decomposed with separation of black oxide of ruthenium. The washed black residue is mixed with the liquid from the coarse heavy grains and scales not acted upon, which are fused for the second and third time with potassa and nitrate of potassa, until at last only oxide of iron remains.

The clear alkaline solution from the osmate of potassa is drained off by means of a syphon from the black residue, and this again washed with hot water containing alcohol. The black mass, which still contains much osmium, is placed in a tubulated retort, with a funnel tube, and to this a receiver is placed, which, with large quantities, is united to some Woulfe's bottles by large tubes filled with a mixture of alcohol and solution of caustic potassa. Concentrated hydrochloric acid is gradually poured through the funnel-tube, and, after the first reaction has ceased, the distillation is continued with aid of heat, as long as osmic acid passes over. It is then, with very careful management on account of the injurious action of the vapor upon the respiratory organs and eyes, dissolved in the solution of potassa, the fluid added to the alkaline solution obtained after the fusion of the ore with caustic potassa and nitrate of potassa, and the whole evaporated until crystals of red osmate of potassa are formed. The rest of the osmium can be precipitated in the mother liquor by chloride of ammonium. (*See* No. 70.)

The dark brownish-red solution in the retort is evaporated to dryness, the mass again dissolved in hot water, and the solution mixed with a hot saturated solution of chloride of potassium in large excess. The iridium, platinum, rhodium, and ruthenium are precipitated as double salts insoluble in the solution, and washed with a saturated solution of chloride of potassium. The iron and palladium remain undissolved.

Residue, B. It is brownish-black, earthy, and rich in rhodium, but contains much silica, alumina, gypsum, iron, &c. To separate these impurities it may be fused with lead and litharge, or with several times its weight of carbonate of soda. In the latter case the mass is first washed with hot water, digested with hydrochloric acid, and then treated as the other residue.

72. THALLIUM.

I. This element was discovered by Crookes in 1861, in a seleniferous deposit from a sulphuric acid manufactory in the Hartz. The name is derived from θαλλὸς, "green," because its existence was first recognized by an intense green line, appearing in the spectrum of a flame in which thallium was volatilized. It was at first suspected to be a metalloid, but further examination proved it to be a true metal. It was first obtained in a distinct metallic form by Crookes towards the end of the year 1861, and about the same time by Lamy, who prepared it from a deposit of the lead chamber of M. Kuhlmann, of Lille.

Thallium is very widely diffused as a constituent of iron and copper pyrites, though it never constitutes more than the 4000th part of the bulk of the ores. It also occurs in some specimens of blende and calamine, sulphide of cadmium, native sulphur; in bismuth, mercury, and antimony ores, and in the manufactured products from these. It is also found in some specimens of lepidolite and mica, and in certain brines, as those of Nauheim, in which it was found associated with chlorides of caseium and rubidium.

II. The easiest mode of extracting the metal consists in treating the thalliferous dust deposited in the flues of the sulphuric acid works before they enter the chamber, with an equal weight of boiling water, drawing off the clear liquor, and treating the undissolved portion again in like manner. The clear liquids are next mixed with a large excess of strong hydrochloric acid, by which a precipitate of impure chloride of thallium is obtained. This is then washed, pressed, and decomposed by treating it with an equal weight of concentrated sulphuric acid. The acid sulphate of thallium thus obtained is dissolved in about 20 parts of water, filtered, and again precipitated as tolerably pure chloride by the addition of hydrochloric acid in excess. The precipitate is washed, pressed, and again converted into sulphate by adding about two-thirds of its weight of oil of vitriol and heating until all the hydrochloric acid is expelled; a dense liquid is thus obtained, which as it cools solidifies to a white mass of acid sulphate of thallium. This is dissolved in about ten times its weight of hot water, filtered, and allowed to crystallize. It may be purified by recrystallization, and if the solution be decomposed by metallic zinc, or by the voltaic battery, pure thallium is abundantly and easily obtained. It may be melted in an iron crucible heated over a gas flame, maintaining a current of coal gas through the crucible to prevent oxidation.

Thallium and its compounds are most easily and certainly detected by spectral analysis. The *spectrum* is characterized by a single bright green line coincident with Ba, δ. It is, however, usually perceptible for but a moment, and its intensity and duration do not safely indicate the amount of thallium present in sulphides, flue-dust, &c.

To find thallium in native sulphur the latter is mostly dissolved by sulphide of carbon, and the residue examined as above. In pyrites, flue dust, and sulphuric-acid chamber sediment, it may be usually detected at once by the spectroscope. The sublimate obtained by strongly heating finely pulverized sulphides in a closed glass tube often gives the reaction when none can be obtained from the substance itself.

III. Thallium is a heavy metal resembling lead in its physical properties. Its specific gravity is 11.81 to 11.91. The freshly-cut surface of the metal has a bluish-white lustre resembling zinc, which quickly tarnishes in the air, a thin film of oxide being formed. It is soft, malleable, and may be pressed into wire, though its tenacity is weak. It produces a streak on paper like graphite. It melts if heated in oxygen, and burns with an intense green flame. It combines directly with chlorine, bromine, iodine, sulphur, and phosphorus. It is very soluble in nitric and sulphuric acids, but the action of hydrochloric is slow even when hot, owing to the insolubility of the chloride. It forms alloys with most of the metals.

Thallium forms two oxides—a protoxide and a sesquioxide. Both the oxides dissolve readily in acids, forming definite crystallizable salts, soluble in water; there are also a few insoluble salts obtained by double decomposition.

IV. Detection.

1. *In the dry way.*—The most characteristic property of thallium is the intense green color which the metal or any of its compounds communicates to a colorless flame. This color examined in the spectroscope appears as one intensely brilliant and sharp green line. The spectral reaction is very delicate, the five-millionth part of a grain of the sulphate being sufficient to produce it. Thallium salts when ignited generally fuse below redness, and then volatilize; some of them, however, as the sulphate and phosphate, will stand a bright red heat without change: the chlorides, on the other hand, distil over with vapor of water. On charcoal before the blowpipe they volatilize, giving an intense green color to the flame.

2. *In solution.*—Salts of the protoxide are for the most part colorless, unless the acid itself is colored. They are mostly soluble in water, neutral to test paper, and have a slight metallic taste. Their aqueous solution is rapidly precipitated in metallic crystals by zinc, and slowly by iron. Hydrosulphuric acid added to a solution of a protoxide salt containing a weak acid, such as carbonic or acetic, separates the whole of the metal in the form of a deep brown sulphide; from solutions of the peroxide salts of the stronger acids, such as the sulphate or nitrate, hydrosulphuric acid precipitates nothing if the acid is in excess, and only a small portion of the metal if the solution is neutral. Sulphide of ammonium precipitates peroxide salt completely, the precipitated sulphide being insoluble in

sulphide of ammonium, in caustic alkalies, their carbonates and cyanides, and only slightly soluble in acetic acid. Hydrochloric acid and soluble chlorides precipitate a difficultly soluble white chloride; hydrobromic acid and bromides precipitate a white nearly insoluble bromide; and hydriodic acid and iodides an insoluble yellow iodide. Alkalies and alkaline carbonates produce no change in salts of the protoxide; phosphate of soda gives a white precipitate, nearly insoluble in ammonia, easily soluble in acids. Chromate of potassa gives a yellow precipitate of chromate of the protoxide. Bichloride of platinum precipitates a very pale yellow insoluble double salt.

From these reactions it appears that in examining a mixed metallic solution, according to the ordinary method of qualitative analysis thallium will be found in the precipitate thrown down by sulphide of ammonium, together with iron, nickel, manganese, &c. From these metals it may be easily separated by precipitating with iodide of potassium, or bichloride of platinum, or by reduction to the metallic state by zinc. Iodide of potassium is—next to the spectral reactions—the most delicate of all tests for thallium.

3. Salts of the sesquioxide are easily distinguished from those of protoxide by their behavior with alkalies, and with soluble chlorides or bromides. Their solutions give, with ammonia, and with fixed alkalies and their carbonates, a brown, gelatinous precipitate of sesquioxide, containing the whole of the thallium. Hydrochloric acid and soluble chlorides or bromides produce no precipitate in solutions of pure salts of the sesquioxide; but if any protoxide is likewise present a sesquichloride or sesquibromide is formed. Chromate of potassa produces no precipitate, except in a solution of sulphate.

V. *Estimation and separation.*—Thallium, when it occurs in solution as a salt of the protoxide, is most conveniently estimated as protiodide, TlI, in which state it is obtained by precipitation with iodide of potassium. The precipitate is quite permanent in the air, and at the temperature of which it is weighed. It is but very slightly soluble in water, insoluble—or nearly so—in saline solutions, alcohol of 92 per cent., and aqueous ammonia; but perceptibly soluble in water containing free acids or fixed alkalies. On mixing the hot ammoniacal solution of a protoxide salt with iodide of potassium, the thallium iodide separates immediately as a curdy precipitate, which, after standing for several hours, may be collected on a weighed filter, and washed with alcohol; or, if this is inadmissible with ammonia, it is then dried at 115°, and weighed—it contains 49.40 per cent. thallium.

Thallium may also be estimated in the form of protosulphate, but not quite so exactly as by the method just described. The sulphate bears a dull red heat without perceptible volatilization, but is volatilized at a bright red heat. Thallium is very completely precipitated from solutions of thallium salts by chloride of platinum; but the precipitated chloroplatinate is troublesome to manage, as it is very finely divided, and is apt to run through the filter when washed with water or alcohol.

In solutions of peroxide salts the thallium may be estimated by reducing the peroxide to protoxide salts with an alkaline sulphite, and then precipitating with iodide of potassium; or by precipitating the thallium with ammonia as sesquioxide, and collecting the precipitate on a weighed filter. The separation of protoxide from peroxide salts may be effected, at least in the case of the chlorides or sulphates, by first precipitating the sesquioxide with ammonia, and then throwing down the remaining portion of thallium from the hot dilute filtrate with iodide of potassium. The separation may also be effected by chloride of platinum, which precipitates only the protoxide salt.

The method of precipitation with iodide of potassium serves also to separate thallium from most other metals, the solution being first mixed with an alkaline sulphite to insure the reduction of any peroxide salt that may be present to the state of protoxide salt. If copper is present the iodide of potassium will throw down copper as well as thallium iodide; but by treating the washed precipitate with ammonia, in contact with the air, copper will be dissolved out, and the thallium will remain as iodide of thallium. The separation of copper from thallium may also be effected, though not so exactly, by precipitating the copper with sulphuretted hydrogen in an acid solution. The same method serves also to separate thallium fromlead and silver. The precipitated sulphides are apt, however, to carry down small quantities of sulphide of thallium.

Small quantities of thallium often occur in bismuth minerals, and preparations are made from them, especially the carbonate. To detect the thallium, the dilute solution of the substance is mixed with a slight excess of carbonate of soda and a small quantity of cyanide of potassium, then gently warmed and filtered. If the bismuth compound contained only 1 pt. of thallium in 100,000, the addition of a few drops of ammonium-sulphide will produce a dark-brown precipitate of sulphide of thallium, which gradually collects together and may be further examined by the spectroscopic method. From carbonate of bismuth, thallium may be easily dissolved out by digestion with cyanide of potassium, less completely with carbonate of soda.

Volumetric Estimation.

Thallium may be estimated volumetrically with permanganate of potassa in the same manner as iron.

For this purpose it must be in the state of a chloride, or of a protoxide-salt mixed with hydrochloric acid, and the solution must not contain more than 1 gramme of thallium in 500 c.c.; the permanganate solution must be more dilute than for the estimation of iron. The titration of the permanganate may be made with pure iron, with thallium, or with a protoxide-salt (the alum, for example); 2 at. iron (112 pts.) correspond to 1 at. thallium (204 pts.), inasmuch as the protochloride HCl is converted by oxidation into a trichloride, HCl_3, so that 1 at. thallium takes up the same quantity of oxygen as 2 at. iron. The solution of the protoxide salt, diluted as above mentioned, is mixed with a few drops of hydrochloric and a few drops of sulphurous acid, and heated to the boiling-point to expel the latter; then left to cool, and mixed with the permanganate.

73. INDIUM.

This metal was discovered in 1863 by Messrs. Reich and Richter, in the zinc blende of Freiberg. It has been investigated since that time by Mr. Clement Winckler, from whose work we borrow the following:—

The zinc obtained from the Freiberg blende contains 0.045 per cent. of indium, as well as small quantities of lead, iron, arsenic, and cadmium. It was by the aid of ammonia, in which the oxide of indium is entirely insoluble, that Reich and Richter separated the indium from the zinc. This process, which is excellent, because the oxide of indium is insoluble in the ammonia, has the inconvenience of being much too expensive, on account of the large quantities of the reagent it is necessary to employ.

I.—*Separation of the Indium.*

a. BY MEANS OF ZINC.—The granulated zinc is dissolved in dilute sulphuric or hydrochloric acid, taking care to leave a small quantity of zinc not dissolved. The solution is heated to the boiling point, and kept there until no trace of gas is discernible. A spongy, metallic substance is obtained in this way, consisting mostly of lead, and which contains, also, arsenic, iron, cadmium, and all the indium of the original zinc, if care has been taken to leave in the liquid an excess of zinc. It can be shown that all the indium is precipitated by testing the filtered liquid with ammonia, adding enough to dissolve the precipitate formed, filtering and examining the residue with the spectroscope.

b. BY MEANS OF ACETATE OF SODA.—This method of separation depends upon the tendency of the indium to form basic salts, a property which belongs to it as much as to the oxide of iron. It is applicable for solutions containing indium and chloride of zinc.

A little sulphuric acid is added to the solution, if it does not already contain it. It is then neutralized with carbonate of soda until the liquid remains cloudy. Acetate of soda is then poured upon it, and boiled for some time. A precipitate is thus formed of basic sulphate of indium, together with iron and a little oxide of zinc, which is filtered and washed. It is preferable to decant it on the filter, the precipitate being gelatinous, and quickly filling the pores of the filter.

c. BY THE MEANS OF CARBONATE OF BARYTA.—The oxide is completely precipitated, even when cold, from its solution by the carbonate of baryta; the liquid should be acidulated by either nitric or hydrochloric acid. It is mixed when cold with carbonate of baryta recently precipitated, stirred for some time, and then the mixture allowed to stand; all the indium will be precipitated with a little oxide of iron, but free from oxide of zinc.

II.—*Purification of Indium.*

After having separated by one of the preceding methods the oxide of indium from the greater part of the zinc, the metal is then purified. Winckler recommends the use of the precipitate obtained by process *a*.

This sponge is dissolved in nitric acid, and the greater part of the lead separated by the aid of sulphuric acid. Hydrosulphuric acid is passed into the filtrate until the lead, cadmium, arsenic, &c., are completely precipitated.

The hydrosulphuric acid is driven off by boiling. The iron is oxidized by adding chlorate of potassa and precipitated by ammonia. The greater part of the zinc remains in solution, the precipitate of oxide of iron and oxide of indium contain very little of it.

After washing, the precipitate is dissolved on the filter in warm dilute acetic acid, and the whole of the indium is precipitated, at the same time a little of the iron and zinc by the hydrosulphuric acid.

It is very difficult to separate all the iron and the zinc, even by repeating the process ten times.

In order to obtain absolutely pure indium it is better to employ the precipitate obtained by the carbonate of baryta. The iron in this case should be in the state of protoxide, because the peroxide of this metal is precipitated by the carbonate of baryta.

The sulphur of impure indium is dissolved in dilute hydrochloric acid. It is heated in order to drive off the hydrosulphuric acid dissolved in the liquid, and a solution is obtained which contains iron in the state of protochloride.

After cooling, a sufficient quantity of carbonate of baryta is added, and is left to digest for twenty-four hours—stirring it frequently:

The precipitate which contains all the indium is carefully filtered and washed, while the whole of the iron and zinc are found in the liquid.

The precipitate is decomposed by sulphuric acid, which gives some sulphate of baryta and some sulphate of oxide of indium, from which the ammonia precipitates entirely pure oxide of indium.

III.—*Preparation of Metallic Indium.*

The oxide of indium is heated to a low temperature in a porcelain crucible, into which a current of hydrogen is passed. A little indium is always lost, on account of the volatility of the metal. If the gas is passed slowly at first, in such a manner that it does not burn between the cover and the crucible, very little of the indium is lost, and the current of gas can then be increased without fear of carrying off much of the metal. The crucible is left to cool in the current of gas, and little metallic globules are obtained at the bottom of the vessel. In order to unite them in one mass fused cyanide of potassium is added—heated to redness—and the union of the globules is aided by inclining the crucible in different directions.

The mass is freed from the cyanide of potassium, which adheres to it, by washing with hot water.

IV.—*Properties of Indium.*

The color of indium is similar to that of platinum, has marked metallic characteristics, and is much softer than lead—can be easily separated into thin laminæ—it marks paper—it does not tarnish on exposure to the air—it is soluble in dilute hydrochloric and sulphuric acid; but, when in contact with concentrated sulphuric acid, is given off sulphurous acid. Nitric acid oxidizes it rapidly. Heated to redness it volatilizes and burns with a violet flame, which deposits a yellow coating on the sides of the crucible. Its specific gravity at 15° is equal to 7.362. Its equivalent, according to Winckler, is 35.9.

V.—*Combinations of Indium.*

The oxide (In O) seems to be the only combination with oxygen. It is honey-colored, and transparent when it is prepared by the calcination of the hydrate: heated it becomes brown.

The calcined oxide is slightly soluble in acids when cold; dissolves rapidly in them when heated.

The salts of indium are white. Zinc precipitates indium from its solution in the form of brilliant scales.

The hydrate of oxide of indium forms a bulky, white precipitate, which resembles aluminum, and yields like this metal a horny mass when dry. It is completely insoluble in ammonia, potassa, and soda.

The carbonate and phosphate of indium are white.

In the solutions of oxides of indium the yellow ferrocyanide of potassium gives a white precipitate.—The red ferridcyanide and sulphocyanide of potassium, gallic acid, and chromate of potassa give no precipitate.

The oxalate of indium is crystalline

The sulphate gives imperfect crystals.

The nitrate crystallizes with difficulty in an aqueous solution.

The very acid solutions give small prisms joined in bundles.

The sulphide of indium is separated in the form of a yellow gelatinous precipitate, which, when dried, gives hard and brittle fragments. The presence of acids prevents the precipitation of indium by hydrosulphuric acid; it is not the same with the sulphide of ammonium. The precipitate obtained by this last reagent is insoluble when cold in an excess of sulphide of ammonium: it dissolves, on the contrary, when heated in this liquid. By cooling the sulphide is precipitated; but it is white in this case, and is probably a hydrate.

74. TELLURIUM ORE.

The Transylvania powdered ore contains graphic and foliated tellurium-ore; *i. e.*, the tellurides of gold, silver, lead, and sulphide of tellurium, mixed with various other minerals.

In order to remove a great portion of the gangue, the finely-powdered ore is mixed with dilute hydrochloric acid, with which it is left in contact until no farther disengagement of carbonic acid takes place, the whole being frequently agitated by stirring. It is then washed and dried. Various methods can be used to extract the tellurium and to recover at the same time the noble metals.

I. The ore is dissolved in nitro-hydrochloric acid, with the precaution, however, that the nitric acid is only gradually added, and in such quantities that it may all be decomposed. When the mass has become completely white, and all the nitric acid has been expelled by heat, some sulphuric and tartaric acids are added, the former to insure the complete precipitation of the lead and the decomposition of the tellurite of lead, the latter to prevent the precipitation of tellurous acid; after this, about twice its bulk is added to the mass. When completely cold, the solution is filtered off and the residue washed. The latter consists of quartz, heavy spar, sulphate of lead, and a small quantity of chloride of silver, which may be extracted by ammonia.

From the solution the gold is precipitated by a concentrated solution of sulphate of protoxide of iron. When the metal has subsided, it is washed and ignited.

The liquor filtered off from it is considerably concentrated by evaporation in a flask, allowed to cool, and mixed with a solution of an alkaline sulphite, when the tellurium is precipitated as a gray powder. After standing for twelve or twenty-four hours it is filtered off, and washed, first with dilute sulphurous acid, and then with water. The solution must be made strongly acid in every case to insure the complete precipitation of the tellurium.

Gold and tellurium may also be precipitated together by an alkaline sulphite, and the latter metal then extracted by means of nitric acid. The filtered liquid is again evaporated to a small bulk, and mixed with an alkaline sulphite, when, in most cases, a farther quantity of tellurium is obtained.

II. The ore, freed from most of the gangue by means of hydrochloric acid, is intimately mixed with twice its weight of bisulphate of potassa; 4 to 6 times its quantity of bisulphate of potassa is then fused in a capacious Hessian crucible at a gentle heat, and into the fusing salt the above-mentioned mixture is introduced by small portions at a time, waiting between each addition, until the frothing of the mass has subsided. When this has ceased, and a sample of the mass being taken out appears quite white, the fused mass is poured off from the gold, which has settled at the bottom of the crucible. The remainder of the salt is then washed out of the crucible with hot water containing sulphuric acid, and the gold collected.

The mass which was poured off is then dissolved in this water, with a farther addition of sulphuric acid, the solution filtered off from the sulphate of lead, &c., and then the silver precipitated by means of hydrochloric acid.

The filtered solution is concentrated by evaporation, and the tellurium precipitated by sulphurous acid.

The tellurium thus obtained is not quite pure. In order to purify it, it is distilled in a tube of hard glass, at a strong red heat, in a current of hydrogen. The traces of lead and copper remain behind as tellurides, and a slight mixture of selenium is carried off by the gas.

Tellurium containing selenium may be easily separated from it completely by fusing it for some time in hydrogen gas. If the two are in solution they are precipitated by sulphurous acid and the selenium, separated by a solution of cyanide of potassium, in which it is soluble. The tellurium remains undissolved. Selenium is precipitated from this solution by acids.

The pulverulent tellurium may be fused easily into a button, if covered with a mixture of 9 parts of chloride of potassium and 7 parts of chloride of sodium.

Accurate quantitative analyses of pure graphic tellurium and foliated tellurium are best made by means of chlorine gas, as in the case of tetrahedrite. Tellurium is volatilized in this process as chloride of tellurium; it requires, however, a very wide tube, on account of its being very bulky.

From the telluride of bismuth (tetradymite) of Schemnitz, in Hungary, the tellurium is best obtained by the following process: The finely-divided ore is intimately mixed with 3 times its weight of ignited cream of tartar, and exposed to a moderate red heat in a covered crucible during one hour, when all the tellurium is converted into telluride of potassium, and the bismuth separated. The cold mass is reduced to powder, thrown on a filter, and completely washed with cold water which has been freed from air by boiling. The dark-red solution of telluride of potassium passing through the filter, when exposed to the air, soon deposits all the tellurium in the form of a gray powder. This method is not applicable to graphic and foliated tellurium ore. It is very useful, however, for the extraction of pure tellurium from the crude tellurium of Vienna, which contains copper, iron, lead, antimony and arsenic. For this purpose, also, a mixture of 4 parts of dry carbonate of soda and 1 part of powdered coal may be used; 2 parts of this mixture are taken for 1 part of the finely pulverized metal; coarsely powdered coal is placed in the bottom of the crucible, the mass pressed down upon this and then covered with the same kind of coal.

The tellurium in the filtrate can be separated from coal, &c., by using an excess of hypochlorite of soda. After long digestion with this reagent, the mixture is heated gradually to ebullition, the chloric acid decomposed by evaporation with hydrochloric acid, and then the tellurium precipitated by sulphurous acid.

75. NATROLITE,* THOMSONITE,† &c.

The amount of water is determined by igniting a weighed quantity of the material, which has previously been dried at 100°.

The finely-divided, unignited mineral, dried at 100, is mixed in a porcelain dish with moderately strong hydrochloric acid, and digested with it, with constant stirring, until completely converted into a gelatinous mass, and all the mineral is dissolved.

This mass is then evaporated to complete dryness, being carefully stirred, in order to render the silica insoluble; the evaporation is best effected, at least towards the end, in the water-bath.

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* Al_2O_3, 3 SiO_2, NaO, 2 HO.

† Al_2O_3, 2 SiO_2, ($\frac{3}{4}$CaO+$\frac{1}{4}$NaO), 2$\frac{1}{2}$ HO.

The remaining salt mass is moistened with hydrochloric acid, after some time a little hot water is poured upon it, and the silica filtered off, washed with hot water, dried, carefully ignited and weighed.

From the filtered solution the alumina is precipitated by sulphide of ammonium, and treated as in No. 16.

When the zeolite contains sesquioxide of iron, the alumina is colored more or less black or greenish-black by sulphide of iron. The iron is separated from it as in No. 21.

The solution filtered from the alumina is evaporated to a small bulk, in a dish, transferred to a weighed platinum crucible, and carefully evaporated to dryness. The saline mass is gradually heated till the sal-ammoniac is volatilized, and finally heated to redness, the cover being loosely placed upon the mouth of the crucible. The residue is chloride of sodium.

The silicic acid obtained in the decomposition of a silicate, especially if it separate rather in a pulverulent than a gelatinous state, must always be examined as to its purity, since it may sometimes contain other constituents of the mineral, especially alumina, or even portions of the undecomposed mineral itself.

Pure silicic acid must entirely dissolve in a boiling solution of carbonate of soda. An insoluble residue indicates an impurity, which should be filtered off and examined. It is preferable, however, to fuse such silicic acid with 3 parts of carbonate of potassa and soda, and to treat it as in No. 79 or 80.

Silicic acid, if perfectly pure, when dissolved in hydrofluoric acid, in a platinum capsule, entirely disappears on evaporation. Should there be any residue, it is again treated with hydrofluoric acid, afterwards with concentrated sulphuric acid, evaporated to dryness, and examined. It sometimes consists of, or contains titanic acid.

76. ILVAITE.*

The finely-powdered mineral is moistened with a suitable quantity of water, in a porcelain capsule, some concentrated hydrochloric acid and a little nitric acid added, and the whole heated to complete gelatinization. The mass is then evaporated to perfect dryness on a water-bath, during which operation it is frequently stirred.

The dry mass is moistened with concentrated hydrochloric acid, then dissolved in chlorine water, the silicic acid filtered off, and treated in the usual manner (No. 75).

From the solution, diluted with the washing-water, the sesquioxide of iron is precipitated by ammonia, the precipitate allowed to subside in a covered vessel, and rapidly filtered off; the solution should first be passed through the filter, which is kept covered, as far as possible, to prevent absorption of carbonic acid. The precipitate is washed by means of the wash-bottle arranged for the purpose, dried, ignited, and weighed as sesquioxide of iron.

The filtrate from the sesquioxide of iron is acidulated with hydrochloric acid, concentrated by evaporation, in a flask, mixed with ammonia, the lime precipitated by oxalate of ammonia, and treated as in No. 12.

The mineral contains about 1.5 per cent. of protoxide of manganese, and 0.5 per cent. of alumina, both of which are contained in the precipitated sesquioxide of iron, and must be separated from it as in Nos. 21 and 25.

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* The compact variety from Elba is not rare. It may also be obtained artificially by fusing together 6 parts of forge-scales, 3 parts of fine white quartz-sand, and 1½ parts of calcined marble, at a strong white heat.

About 1.5 per cent. of water is also present as an unessential constituent; its quantity may be ascertained by ignition in a covered crucible.

In order to ascertain directly the relative amounts of protoxide and sesquioxide of iron, the process described in No. 24 must be followed.

77. CHRYSOLITE (OLIVINE).

$$2\,(MgO, FeO), SiO_2.$$

The very finely-powdered mineral is decomposed by digestion with concentrated hydrochloric acid, the mass dried upon the water-bath, moistened with concentrated hydrochloric acid, and, after some time, mixed with water and filtered from the separated silica.

Small amounts of copper and tin, which are contained in many specimens of olivine, are detected and separated by mixing the solution with saturated sulphuretted hydrogen-water, until it smells strongly, and allowing it to stand for some time in a closed vessel.

The solution filtered from the precipitate is concentrated by evaporation, some chlorate of potassa being added to peroxidize the iron.

The sesquioxide of iron may be precipitated by an excess of ammonia, and the magnesia separated from it by boiling the solution until all the free ammonia is expelled, when the sesquioxide of iron remains, and may be filtered off.

This filtrate contains, besides magnesia, a small quantity of protoxide of manganese and protoxide of nickel, which latter is wanting only in the olivine of meteoric iron. These are precipitated by sulphide of ammonium, an excess of which is, as far as possible, to be avoided. The precipitate is not to be filtered off until it has separated so as to leave the solution perfectly clear; it may then be washed with very dilute sulphide of ammonium. If both metals are present only in small quantities, the sulphide of manganese may then be separated from the sulphide of nickel by treating it, upon the filter, with very dilute hydrochloric acid, in which the sulphide of nickel is, practically, insoluble. The small quantity of sulphide of nickel is then ignited in the air, and weighed as protoxide. The manganese is precipitated from the solution by carbonate of soda, at a boiling heat.

The liquid filtered from the precipitate produced by sulphide of ammonium, is mixed with ammonia, and the magnesia precipitated by phosphate of soda (No. 6).

In the analysis of olivine, the iron, when converted into sesquioxide, may also be separated from the other bases by succinate of ammonia (No. 21).

78. DATOLITE.

$(3\ CaO, 3HO, BO_3)\ SiO_2$.

For the determination of water, a weighed quantity of the mineral is heated to bright redness.

If the unignited mineral, in a finely-powdered state, be digested with moderately strong hydrochloric acid, it becomes a gelatinous mass. If the mixture be heated to boiling, and filtered while hot, boracic acid separates from the solution in crystals.

The finely-powdered mineral is decomposed by digestion with hydrochloric acid, and the mass evaporated to dryness, when a great part of the boracic acid is volatilized; after exposure for a considerable time to a temperature of 100°, the residue is heated with water containing hydrochloric acid, the silicic acid filtered off, washed, dried and ignited.

The filtrate is neutralized with ammonia, and the lime precipitated by oxalate of ammonia (No. 12).

By this process the boracic acid cannot be determined directly but only by difference, because a large part of it volatilizes during evaporation. In order to make a direct determination, the mineral is decomposed by hydrochloric acid, or a retort furnished with a receiver, distilled to dryness, and the distillate containing the boracic acid poured back upon the residue, with which it is digested for some time, and then filtered from the silicic acid. The lime is then precipitated by a large excess of oxalate of potassa, filtered, and the filtrate concentrated by evaporation. From this the boracic acid is precipitated as a double fluoride of boron and potassium. For this purpose it is placed in a platinum dish with a little potassa, then mixed with a small excess of hydrofluoric acid, and evaporated to dryness. For the separation of the other salts, the mass is treated with a moderately concentrated solution of acetate of potassa, allowed to stand for some time, and the double fluoride of boron and potassium thrown upon a weighed filter, and washed with the solution of the acetate. The acetate of potassa is then washed out with alcohol. The double fluoride is dried at 100° and weighed.

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79. ULEXITE.

$$NaO, 2BoO_3 + 2\,(CaO, 2BoO_3) + 18HO.$$

After determination of the water the mineral is dissolved in hydrochloric acid, neutralized with ammonia, and the lime precipitated by oxalate of ammonia. The filtered solution is concentrated by evaporation, and the boracic acid separated as in No. 78 as a double fluoride of boron and potassium.

For the determination of the soda another portion is dissolved, the lime precipitated by oxalate of ammonia, the filtrate evaporated to dryness, and heated to drive off the ammoniacal salts. The mass is then digested with strong hydrofluoric acid, evaporated to dryness, digested with concentrated sulphuric acid, and evaporated to drive off the fluoride of boron. The sulphate of soda is finally ignited, a piece of carbonate of ammonia being held in the crucible.

80. ORTHOCLASE.

$$KO, SiO_2 + Al_2O_3, 3SiO_2.$$

I. The very finely-powdered and levigated mineral, dried at about 200°, is very intimately mixed, in a capacious platinum crucible, with 4 or 5 parts of carbonate of baryta; the crucible is then inclosed in an earthen crucible, which is placed in a wind-furnace with a good draught, and exposed for at least half an hour to an intense white heat, so that the contents may be firmly aggregated into a cinder-like mass. The decomposition takes place more rapidly, and with greater certainty, when the crucible is exposed to a blowpipe flame, so that the mass fuses completely.

Or the mineral is mixed, in a silver crucible, with 4 parts of hydrate of baryta, previously freed by heat from its water of crystallization, and the mixture heated to fusion.

The mass is then turned out of the crucible into a capacious dish, a quantity of water poured over it, and hydrochloric acid gradually added in slight excess, until, with the aid of a gentle digestion, it is completely decomposed and dissolved, with exception of some gelatinous silicic acid which is separated. The whole solution is then evaporated to perfect dryness, in order to render the silicic acid insoluble, the evaporation being conducted towards the last upon a water-bath, with constant stirring.

The saline mass is afterwards moistened with hydrochloric acid, a proper proportion of water added, and, after digestion, the silica filtered off, washed, thoroughly dried, ignited, and weighed in a covered crucible.

From the solution the baryta is precipitated by gradual and cautious addition of dilute sulphuric acid, a great excess of which is to be carefully avoided; the sulphate of baryta is then filtered off and washed. (*See* No. 3.)

The filtrate is concentrated, if need be, by evaporation, the alumina precipitated by sulphide of ammonium, and treated as in No. 16.

The liquid filtered from the alumina is evaporated to dryness, and the dry mass ignited to expel the ammoniacal salts. This process requires so much the more care, to avoid spirting, the more sulphate of ammonia it contains, in consequence of the careless addition of sulphuric acid.

At the end of the operation, in order to convert any alkaline bisulphate into neutral sulphate, a fragment of carbonate of ammonia is held in the covered crucible.

The residue is sulphate of potassa, and is weighed as such. Should soda also be present in the mineral, the residue must be treated as in No. 4.

Another method consists in precipitating most of the baryta from the original solution by gradually and cautiously adding dilute sulphuric acid; the rest of the baryta, together with the alumina, is then precipitated by a mixture of carbonate of ammonia and free ammonia, added in slight excess.

After twenty-four hours, the precipitate is filtered off, washed, the alumina (together with the baryta) extracted by dilute hydrochloric acid, precipitated by freshly-prepared sulphide of ammonium, and rapidly washed, with as little exposure to air as possible.

The liquid containing the alkali, filtered off from the precipitate produced by carbonate of ammonia, is concentrated by evaporation, acidified with hydrochloric acid, evaporated to dryness, and the saline mass heated in a covered crucible ultimately to redness; the residue is chloride of potassium (or chloride of sodium). It must be tested for baryta with sulphuric acid, since carbonate of baryta is not absolutely insoluble, and would have been converted into chloride of barium by ignition with salammoniac.

II. A second method of decomposing feldspar is that with hydrofluoric acid. The levigated mineral is placed in a platinum dish, or in a capacious platinum crucible, mixed with a suitable quantity of fuming hydrofluoric acid, and digested with it to complete decomposition.

Or the mineral may be spread out in a shallow platinum capsule, moistened with water, and exposed for a long time to the vapor of hydrofluoric acid, in an appropriate leaden vessel closed with a lid. The hydrofluoric acid is evolved from powdered fluor-spar, which is placed at the bottom of the vessel, moistened with concentrated sulphuric acid, and gently heated.

The mineral is however most easily decomposed by fluoride of ammonium. One part of the mineral is mixed with about six parts of the fluoride with a little water, digested for some time and then raised to a low red heat.

When the decomposition of the feldspar is completed, the mass is gradually and cautiously mixed with pure concentrated sulphuric acid, and evaporated, slowly and carefully, to dryness. All the fluorine and silicon are thus expelled, and after the volatilization of the excess of sulphuric acid, the bases remain as sulphates.

The dry mass is moistened with concentrated sulphuric acid, and after a little time mixed with water, in which, if the decomposition be complete, it should entirely dissolve.

From this solution the alumina and alkalies are separated as directed above.

A small quantity of iron, which is frequently present, is to be sought in the alumina.

In the analysis of a feldspar containing lime (labradorite, anorthite). the latter is precipitated, after the separation of the alumina, by oxalate of ammonia.

When petalite and spodumene are analyzed by the above methods, a mixture of salts of soda and lithia is obtained at last, and must be analyzed as in the case of triphylline.

III. Silicates are easily decomposed by acids, if melted to a glass with a small quantity of precipitated carbonate of lime in a platinum crucible before the gas blowpipe. One part of feldspar is mixed with 0.4 parts of carbonate of lime.

In order to find the amount of alkalies in silicates not easily decomposed by acids, they are mixed with five to six of carbonate of lime and about three-fourths chloride of ammonium and ignited, when the alkali may be extracted with water.

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81. PYROXENE, AMPHIBOLE, GARNET, IDOCRASE, EPIDOTE.

Silcates of CaO, MgO, FeO, MnO and Al_2O_3.

The very finely-powdered mineral must be decomposed by fusion with four parts of carbonate of potassa and soda.

The mass is softened with water, dissolved in hydrochloric acid, the silica rendered insoluble by evaporation, as in the analysis of feldspar; the dry mass moistened with hydrochloric acid, and a little nitric acid, warmed, diluted, and the silicic acid filtered off.

The solution is then neutralized by carbonate of soda, acetate of soda added and heated to boiling. The iron and alumina are precipitated, and may be separated by hyposulphite of soda, as in No. 21.

The filtrate, which contains acetates of lime, magnesia, and manganese is saturated while hot with chlorine gas, which precipitates the manganese. After ignition it is weighed as MnO, Mn_2O_3. If the fluid has been colored red by the formation of permanganic acid, ammonia is added, and then boiled until the color is destroyed. The lime and magnesia are separated in the filtrate as in No. 12.

These and all similar minerals, not attacked by hydrochloric acid, may likewise be conveniently decomposed by hydrofluoric acid; in which case, however, the silica must be determined by loss. (*See* Orthoclase.)

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82. BERYL.

$$Be_2O_3, 2\,SiO_2 + Al_2O_3, 2\,SiO_2.$$

The very finely-powdered mineral, previously well dried, is fused in a platinum crucible with 4 times its weight of carbonate of potassa and soda (*see* No. 10); the mass is softened with water, digested with excess of hydrochloric acid until the decomposition is complete, and evaporated to perfect dryness to render the silica insoluble. The residue is moistened with hydrochloric acid, and treated with warm water; the silica is then filtered off, the solution concentrated by evaporation, and dropped very gradually, with constant stirring, into an excess of a warm concentrated solution of carbonate of ammonia, which precipitates the alumina, and dissolves the berylla (glucina). When the precipitate has been digested for some time with the solution in a closed vessel, the solution is filtered off, boiled for a long time, until the greater part of the carbonate of ammonia is expelled, slightly acidified with hydrochloric acid, digested for some time to expel the carbonic acid, and the glucina finally precipitated by caustic ammonia.

Pure glucina may be prepared in the following manner. The mineral is heated to redness, and then thrown into cold water, when it may be more easily pulverized. 7 parts of the powder are mixed with 13 parts of finely-powdered fluor spar, and 18 parts of concentrated sulphuric acid, and warmed until no more fluoride of silicium is given off. The mass is then gently ignited, digested for some time with water, and the sulphate of lime filtered off. 2 parts of sulphate of potassa are then added and the solution evaporated to crystallization, when the greater part of the alumina crystallizes as alum. Acetate of soda is then added to the solution, and by boiling the remainder of the alumina and the sesquioxide of iron are precipitated. The glucina is precipitated from the filtered solution by ammonia.

If hyposulphite of soda precipitates alumina alone, and no glucina, in a neutral solution of the two bases, this method may be used for their separation.*

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* See Silliman's Journal, vol. xxxvi., Prof. C. A. Joy on Glucinum and its Compounds.

83. TOPAZ.*

$$6\,(3\,Al_2O_3,\,2\,SiO_2)+(3Al_2F_3+2\,SiF_4).$$

At a very intense white heat, the topaz loses all its fluorine in the form of tetrafluoride of silicon. (23 per cent.)

When fused, in the state of very fine powder, with 4 times its weight of anhydrous carbonate of soda, it is decomposed, with formation of fluoride of sodium, which is extracted by water. Before filtering off the residual silicate of alumina, however, the solution should be digested with some carbonate of ammonia, in order to precipitate any small quantities of alumina and silica which may have been dissolved.

The residue is then filtered off, washed with dilute carbonate of ammonia, and farther treated as in No. 75.

The alkaline filtrate is concentrated and freed from ammonia by evaporation, and the greater part of the carbonate of soda neutralized by nitric acid, so that some carbonate may still remain undecomposed. The solution is then mixed with chloride of calcium, which precipitates a mixture of carbonate of lime and fluoride of calcium. When the precipitate has separated, by the aid of a gentle heat, it is filtered off, washed, and ignited. The carbonate of lime is then dissolved in dilute acetic acid, the solution evaporated to dryness on a water-bath to expel the excess of acid, and the acetate of lime extracted from the dry mass with hot water. The residual fluoride of calcium is filtered off, washed, dried, ignited, and weighed. If the precipitate of carbonate of lime and fluoride of calcium had not been ignited previously to the treatment with acetic acid, the fluoride would have entered the pores of the filter, and the filtrate would have been turbid.

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* Defective crystals of Bryzilian topaz may frequently be obtained at a cheap rate.

84. FLUORITE.

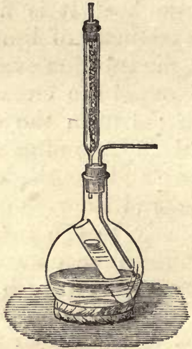
CaF.

A weighed quantity of the finely-powdered mineral is mixed, in a platinum crucible, with concentrated sulphuric acid, and heated until all the hydrofluoric acid is expelled, and the greater excess of sulphuric acid volatilized. The residual sulphate of lime is then mixed with alcohol, filtered off, washed with alcohol, ignited and weighed. Or it may be dissolved in water containing hydrochloric acid, the solution mixed with ammonia, and the lime precipitated by oxalate of ammonia.

The fluorine is determined from the loss. In order to estimate it directly, the decomposition must be effected in a platinum retort, the vapors of hydrofluoric acid conducted into solution of carbonate of soda, and the fluorine precipitated from the solution by chloride of calcium, as in the analysis of topaz.

Or the very finely-powdered mineral may be mixed with an excess—that is, with at least an equal weight—

Fig. 15.



of finely-powdered silicic acid (that prepared from tetrafluoride of silicon is the best), the mixture introduced into an apparatus similar to that employed in alkalimetry, and the sulphuric acid, which must for this purpose be very concentrated, allowed to flow upon it. With the aid of a gentle heat, tetrafluoride of silicon is formed, which is allowed to escape in the gaseous state through a tube filled with chloride of calcium; the last portions are withdrawn from the apparatus by sucking air through it, for which purpose, there is attached to the chloride-of-calcium-tube a small tube filled with fragments of moist hydrate of potassa, through which the air is drawn. The loss of weight expresses the amount of tetrafluoride of silicon which has been evolved.

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85. CRYOLITE.*

$$3\,NaF + Al_2F_3.$$

The analysis may be made by means of concentrated sulphuric acid as in the case of fluorite. The fluorine is determined by the loss. For the direct determination, the mineral is decomposed in a platinum retort, and the fluorine contained as fluoride of calcium, as with fluor-spar and topaz. The excess of sulphuric acid is driven off by heat from the residue, which is completely soluble on being digested in water, if the decomposition was complete. The alumina is precipitated by carbonate of ammonia. The filtered liquid is then evaporated to dryness, placed in a platinum crucible and carefully raised to a red heat with the precaution that nothing is thrown out from the crucible by the decomposition of the sulphate of ammonia. A small piece of carbonate of ammonia is held in the crucible and allowed to evaporate slowly. The residue is weighed as neutral sulphate of soda.

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* This remarkable mineral is found in an immense deposit 80 feet thick and 300 feet long in Greenland at the head of Arksut Bay, near Cape Farewell. It is often associated with crystals of galena, spathic iron, copper and iron pyrites, etc.

The Pennsylvania Salt Company introduced to our country this valuable material, and now prepare from it caustic soda, carbonates and other salts of soda, sulphate of alumina, etc.

One hundred pounds of cryolite yield 44 pounds dry caustic soda; or 75 pounds dry carbonate of soda, 203 pounds crystallized carbonate soda; or 119½ pounds bicarb. soda, and 24 pounds of alumina.

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86. ZIRCON.

ZrO_2, SiO_2.

A carefully-selected specimen of zircon which has been ignited, and thus deprived of color, is levigated to a very fine powder, and fused, at a good heat, in a platinum crucible, with 4 parts of anhydrous carbonate of soda. The mass is digested with water, which dissolves the silicate of soda, and leaves a silicate of soda and zirconia as a crystalline powder; this is washed and decomposed by digestion with concentrated hydrochloric acid. The mass is dried up in a water-bath, treated with water containing hydrochloric acid, the silica filtered off, and the zirconia precipitated by ammonia.

If the zirconia contain any iron, the precipitate is digested with oxalic acid, which dissolves the sesquioxide of iron, leaving oxalate of zirconia, at least the greater part, undissolved.

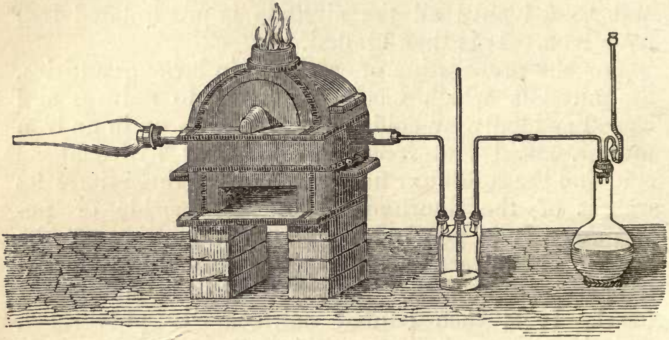
Or the precipitate may be treated with sulphide of ammonium, to convert the iron into sulphide, the solution once more decanted, and the black precipitate treated with solution of sulphurous acid, which immediately dissolves the sulphide of iron leaving the zirconia colorless. For quantitative analysis the solution containing zirconia and iron, after neutralization, is mixed with hyposulphite of soda, and heated until all the zirconia is precipitated free from iron. It is then ignited.

For the preparation of zirconia in large quantities, the zirconia which has been heated to redness and cooled suddenly by cold water is broken up in an iron mortar, sifted and freed from iron by hydrochloric acid and the residuum fused with two or three times its weight of the fluorhydride of the fluoride of potassium. It is gently heated at first to drive off the water and afterwards when dry and hard, the temperature is raised until the mass is completely fused. It is then poured out, coarsely pulverized, and heated to boiling with a little water mixed with hydrofluoric acid. The solution of fluozirconate of potassium, which is very soluble in hot water filtered off from the fluosilicate of potassium, the latter being washed with hot water. On cooling the salt crystallizes in fine prisms. It may be purified by recrystallization. Heated with sulphuric acid, it is converted into a double sulphate, which leaves after strong ignition pure zirconia mixed with sulphate of potassa.

The ignited zirconia is again rendered soluble by heating for a long time with concentrated sulphuric acid, or with acid fluoride of ammonium. It is completely precipitated from a neutral solution, by a boiling saturated solution of sulphate of potassa, as a white pulverulent double salt. After boiling this precipitate is scarcely soluble in water or even in acids.

The chloride of zirconium, $Zr\,Cl_2$, can be prepared directly from zircon, as a white sublimate soluble in water, if the very finely levigated mineral with several parts of pure sugar is ignited, and the mass, while hot, introduced into a tube of very hard glass, in

Fig. 16.



which it is heated to full redness, while a stream of dry chlorine gas is passed over it. The chloride of silicon passes off as gas, while the chloride of zirconium sublimes in the cooler part of the tube.

87. CERITE.*

$$2\,(CeO, LaO, DiO), SiO_2 + HO.$$

Cerite, in fine powder, is treated with concentrated sulphuric acid, with which it is digested, until the high temperature produced by the combination has caused it to form a dry mass.

Cold water is then poured over it, and the mixture allowed to digest, in the cold, until the sulphates are dissolved. The solution filtered from the silica, which must be concentrated by evaporation if too largely diluted by the washings, is mixed with a boiling saturated solution of sulphate of potassa, and allowed to cool. Cerium, lanthanum and didymium are thus precipitated as double sulphates, while iron, &c., remain dissolved. The precipitate is filtered off, and washed with a saturated solution of sulphate of potassa. Crystalline crusts of sulphate of potassa are placed in the filtrate, and in this way the remainder of the double salt is precipitated.

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* Only to be found in one locality—the mine of Bantnäs, near Riddarhytta in Westmanland. May be obtained from dealers in Minerals, or from Stockholm.

The precipitated salt is dissolved in the necessary quantity of boiling water, with the addition of some hydrochloric acid, and the bases precipitated from the hot solution by an excess of caustic potassa. (Ammonia precipitates basic salts.) Or the double salt is mixed with pure lamp-black and starch paste, covered with coarsely pulverized charcoal and heated to redness for one hour.

The sulphide of potassium formed is completely washed out with water, the sulphide of cerium dissolved in nitric acid, evaporated to dryness and ignited.

After ignition, they appear as a cinnamon-brown powder. When converted into sulphates by digestion with concentrated sulphuric acid, they give, with water, a yellow solution, from which sulphate of potassa precipitates a lemon-yellow mixture of double salts.

Another method of obtaining the oxide of cerium consists in precipitating the original sulphuric solution, while hot, with an excess of hydrate of potassa, washing the precipitate, and digesting it with an excess of solution of oxalic acid, when the iron and lime are dissolved, and the oxide of cerium, &c., left as white oxalates, which are filtered off and washed. By ignition in air, they are converted into the brown oxides.

There is at present no method of accurately separating these three oxides from each other.

THE HYDRATED PROTOXIDE OF CERIUM is colorless, but oxidizes rapidly on exposure to air, and becomes yellow. It is obtained by igniting the carbonate or oxalate in a current of hydrogen, is bluish-gray, and oxidizes in the air to a yellowish-white compound of oxide and sesquioxide, or by heating to an orange-red. It is insoluble in nitric and hydrochloric acids, but soluble in sulphuric with a yellow color.

THE SESQUIOXIDE OF CERIUM, in the pure state, is yellow, with a tinge of red; when impure, it is brick-red. It is produced when the hydrate is ignited in air. The sesquioxide is soluble only in hot concentrated sulphuric acid; the solution has a fine yellow color. The hydrated sesquioxide is dissolved, in quantity, with a yellow color, by the alkaline bicarbonates, especially by bicarbonate of ammonia. The sesquioxide is insoluble in concentrated hydrochloric acid, but on addition of alcohol, it is dissolved in the form of protochloride.

OXIDE OF LANTHANUM is colorless; when heated with water, it is converted into the hydrate, which has an alkaline reaction. It is dissolved by a hot solution of chloride of ammonium, with evolution of ammonia. Its salts are colorless. The carbonate is insoluble in carbonate of ammonia.

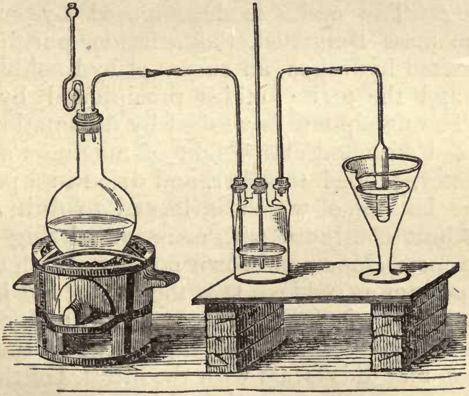
OXIDE OF DIDYMIUM, when ignited, is brown. When exposed to a white heat it assumes a dingy white color, with a tinge of green. It is soluble in acids; its salts have the color of amethyst, with a tinge of blue; with hydrate of potassa they yield a violet hydrate. The carbonate is insoluble in carbonate of ammonia.

The ignited brown mixture of the three oxides is dissolved by hydrochloric acid, with evolution of chlorine.

If the mixed hydrates, precipitated by potassa, be dissolved in nitric acid, the solution evaporated to dryness, and ignited, a dark brown oxide is obtained, from which a part, at least, of the oxide of lanthanum may be obtained in a pure state. For this purpose, the finely-powdered oxide is mixed with water, to which nitric acid, free from nitrous acid, is added in single drops with continual agitation, in proportion as it is saturated. From the filtered solution, at a boiling heat, carbonate of ammonia precipitates carbonate of oxide of lanthanum in shining, crystalline scales.

When the oxides precipitated by potassa are mixed with a concentrated solution of potassa, and the latter saturated with chlorine gas, and frequently agitated, the cerium is converted into an insoluble yellow compound of the sesquioxide, while didymium and lanthanum, together with some cerium, are dissolved as protochlorides. The yellow sesquioxide of cerium is digested still longer with chlorine-water, filtered off, washed, and digested with dilute potassa to remove

Fig. 17.



hypochlorous acid; any potassa which it has taken up is then extracted by dilute nitric acid. The solution of the protochlorides (of didymium and lanthanum) is again precipitated by potassa, and the precipitate treated a second time with potassa and chlorine-gas.

The oxide of cerium can be obtained nearly pure if the mixed oxides are first treated with dilute and then with concentrated nitric acid, which dissolves out the lanthanum and didymium. The solution is evaporated, the salt ignited, and the oxide again treated with very dilute nitric acid. The oxide of cerium remains undissolved.

From the solution the didymium and lanthanum are precipitated by ammonia and dissolved in sulphuric acid. If the dried mixture of salts is dissolved in water until it is saturated at 5° or 6°, and this solution heated to 30°, the sulphate of the oxide of lanthanum separates, while the didymium remains in solution. By repeating the operation both salts may be obtained in a pure state. The salt of lanthanum is colorless, and that of didymium dark rose-red.

Another method of approximate separation is the following. The cerite is decomposed by sulphuric acid, the mass lixiviated, the solution purified with sulphuretted hydrogen, an excess of hydrochloric acid added, and the cerite oxides precipitated by oxalic acid. The precipitate is washed by decantation, dried and mixed with half its weight of magnesia alba and some water, rubbed together, and dried in a porcelain dish, the bottom of which is heated to dull redness, and the heat continued with constant stirring until it has become a cinnamon-brown powder, which contains all the cerium as oxide. It is then dissolved in warm concentrated nitric acid. The deep brownish-red solution contains a double salt of the nitrate of the oxides of cerium and didymium with the nitrates of the oxide of lanthanum and magnesia, which may be obtained in deep reddish-yellow rhombohedral crystals. The red solution is evaporated to a syrupy consistency, and a large excess of boiling hot water containing some nitric acid is poured over it, which precipitates alone the basic nitrate of the oxide of cerium, which is washed by decantation with hot water mixed with nitric acid, as it is quite soluble in pure water. The mother liquor and wash water are concentrated to a syrup and again treated in the same manner.

This last mother liquor usually contains only lanthanum, didymium and magnesia, and is generally colored violet, which color is destroyed by alcohol and other reducing agents. After concentration, crystals of double salts of these bases are formed.

The metal cerium was obtained by the following process: a solution of the brown oxide of cerium in hydrochloric acid was mixed with an equivalent quantity of chloride of potassium and of chloride of ammonium, and the whole evaporated to dryness. The mass was then transferred to a platinum crucible, and heated until the whole of the chloride of ammonium was volatilized and fusion obtained. The fused mass was poured out, coarsely powdered, and mixed, while still warm, with fragments of sodium, and introduced into an earthen crucible previously heated to redness. When the contents had again fused, and the excess of sodium volatilized, the crucible was removed from the fire; the deep gray resulting mass was filled with little metallic globules. In a second experiment a large piece of sodium was thrown into a red-hot crucible containing chloride of potassium, and then the coarsely powdered chloride used as before. In operating in this way, a larger proportion of metallic globules was obtained, some of which weighed from 50 to 60 millegrams. These metallic globules appear to consist principally of cerium. The color of the metal is intermediate between the color of iron and that of lead. The metal is lustrous when polished, and malleable. Its density is about 5.5 at 12°. Exposed to the air it loses its lustre, and becomes slightly blue. It feebly decomposes water at 100°. Hydrochloric acid dissolves it with energy; concentrated nitric acid converts it into a clear brown oxide; the dilute acid dissolves it. By evaporation a white salt is obtained, which leaves, after calcination, a brown oxide, insoluble in nitric acid and in dilute sulphuric acid. Concentrated sulphuric acid slowly dissolves this oxide, forming a yellow solution, which shows the reactions of ceric salts. Hydrochloric acid dissolves this oxide with disengagement of chlorine, forming a colorless solution. When a globule of cerium is heated by the blowpipe to dull redness, the metal inflames and burns vividly, forming brown oxide; but upon submitting a globule suddenly to a very high temperature, it burns with explosion, sending out bluish sparks. Cerium powder can inflame below 100°.

88. GADOLINITE.*

$$YO, CeO, LaO, ErO, CaO, MgO, MnO, FeO, Fe_2O_3, Al_2O_3, SiO_2.$$

The finely-powdered mineral, dried at 100°, is decomposed by digestion, in a porcelain dish, with concentrated hydrochloric acid, to which some nitric acid has been added, to peroxidize the iron; the mass is completely dried up, with frequent stirring, in a water-bath, and maintained for some time at that temperature.

It is then digested with a little water acidulated with hydrochloric acid, the silica filtered off, washed with hot water, thoroughly dried, ignited and weighed.

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* This rare numeral varies in composition according to the locality in which it is found. All specimens contain yttria, oxides of cerium, iron and silica as the ingredients, many, glucina and small quantities of lime, magnesia and manganese.

The solution is neutralized by ammonia, chloride of ammonium added, and the yttria, together with oxides of cerium and lanthanum are precipitated by oxalate of ammonia. Glucina, oxides of iron and manganese remain in solution, to be separated afterwards.

The filtered and washed mixture of the three oxalates is ignited to decompose the oxalic acid, the oxides dissolved in a very little hydrochloric acid, and the solution mixed with a hot saturated solution of sulphate of potassa, which precipitates the oxides of cerium and lanthanum as a white double sulphate. After the lapse of twenty-four hours this is filtered off, and thoroughly washed with a saturated solution of sulphate of potassa, in which it is perfectly insoluble. It is then treated as in No. 87.

The yttria is then precipitated from the filtered solution by oxalate of ammonia. In order to separate the lime, it is dissolved in hydrochloric acid, and precipitated by ammonia.

In order to detect the presence of glucina in yttria, it is necessary, since the latter cannot be extracted by caustic potassa, to mix the precipitate with pure sugar, and to carbonize the mass in a platinum crucible; it is then ignited in a stream of dry chlorine-gas, when the chloride of glucinum sublimes, and the chloride of yttrium remains in the carbonized mass.

The following method* has been proposed for the separation of yttria and erbia:—

The precipitate formed by oxalic acid, in the solution obtained by heating gadolinite with hydrochloric acid, contains the oxalates of erbium and yttrium, besides those of calcium, cerium, lanthanum, and didymium, with traces of oxalate of manganese and silica. These oxalates are converted into nitrates; the solution is treated with sulphate of potassa, with the usual precaution (i, 831), to separate the cerium metals; the erbium and yttrium, which still remain in solution, are again precipitated by oxalic acid; the oxalates are ignited; and the residual oxides, after being carefully freed from admixed carbonate of potassa by boiling with water, are dissolved in nitric acid, and again precipitated from the acid solution by oxalic acid, this series of operations being repeated till the solution of the mixed earths in nitric acid, when examined in the spectral apparatus, no longer exhibits the absorption-bands characteristic of didymium. The last portion of calcium and magnesium are separated by precipitating the acid solution of the mixed earths with ammonia, the calcium and magnesium then remaining in solution; the precipitate is dissolved in nitric acid; and the solution, now containing nothing but erbia and yttria, is precipitated by oxalic acid.

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* **Method Bahr and Bunsen.**

To separate erbia and yttria, the oxalates are converted into nitrates; the solution is evaporated in a platinum dish, till the first bubbles of nitrous acid make their appearance; and the dish is quickly cooled by placing it in cold water, whereupon the viscid mass solidifies to an extremely brittle glass. On dissolving the mass in a quantity of warm water just sufficient to prevent the solution from becoming turbid on boiling, nitrate of erbium, still containing yttrium, separates on slow cooling in needles, which must be separated from the mother liquor by decantation and quickly rinsed with water containing about three per cent. of nitric acid. This mother liquor, treated in a similar manner, yields a second crop of crystals of nitrate of erbium containing yttrium; the mother liquor of this yields a third crop, and so on, the proportion of nitrate of yttria in the successive crops of crystals continually increasing. By mixing a certain number of the earlier and comparatively pure crops of crystals, and treating them in a similar manner, products are obtained of still greater purity; and by repeating this mode of treatment several times, nitrate of erbium is ultimately obtained containing no appreciable quantity of yttrium.

Pure erbia obtained by ignition of the nitrate or oxalate, has a faint rose-red color (not yellow, as stated by Mosander). It does not melt at the strongest white heat, but aggregates to a spongy mass, glowing with an intense green light; which, when examined by the spectroscope, exhibits a continuous spectrum intersected by a number of bright bands. Solutions of erbium-salts, on the other hand, give an absorption-spectrum exhibiting dark bands, and the points of maximum intensity of the light bands in the emission-spectrum of glowing erbia coincide exactly in position with the points of greatest darkness in the absorption-spectrum. The position of these bands is totally different from those in the emission and absorption-spectra of didymium; in fact there is not a single line of the erbium-spectrum which corresponds with that of didymium.

89. THORITE.*

$ThO_2, SiO_2 + 2\,HO$.

The finely-powdered mineral gelatinizes entirely with concentrated hydrochloric acid. The solution is evaporated to dryness, the silica filtered off, the filtrate highly concentrated by evaporation, and mixed with a boiling saturated solution of sulphate of potassa. In this way all the thoria, like the oxides of the cerium-class, is precipitated as a white pulverulent double salt. After cooling, this is filtered off, and washed with a saturated solution of sulphate of potassa. There remains in the solution the unessential elements of the mineral, iron, manganese, lime, magnesia, alumina, and the alkalies. It is then dissolved in boiling water and the alumina precipitated by caustic potassa.

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* This black, amorphous mineral, from Lövön, near Brevig in Norway, is taken here, without regard to its rarity, as an example of a compound of thoria, in order to direct attention to the detection of this earth, which must certainly occur more frequently. The orange-colored orangite of Brevig has a similar composition.

After ignition, thoria is white, and has a spec. grav. of 9.4. It can only be dissolved in hot concentrated sulphuric acid. The hydrate of thoria is insoluble in potassa.

Chloride of thorium is fusible, and may be sublimed.

Sulphate of thoria dissolves but slowly in water. When the solution is heated, a tissue of fine crystalline needles separates, consisting of salt containing less water, which is very sparingly soluble.

90. TRIPHYLITE.

$3 (FeO, MnO, MgO, LiO) PO_5$.

Besides the principal constituents this mineral contains small quantities of silicic acid, lime, potassa, and soda. For analysis it is dissolved in hot nitric acid, the silicic acid filtered off, a few grains of mercury dissolved in the filtrate, evaporated to dryness on the water-bath, moistened with water, and again evaporated to drive off all the free acid. The mass is then lixiviated with hot water, which dissolves all the bases, the phosphoric acid remaining in the residue. This is fused with carbonate of soda and potash, as in the case of apatite. The alkaline phosphate is dissolved in water, the oxide of iron filtered off, and the phosphoric acid precipitates as a double salt of magnesia.

The solution which contains the bases, is evaporated, and heated to a dull red heat to drive off the quicksilver. The mass is then treated with a solution of nitrate of ammonia to dissolve the lime and magnesia, and the oxides of iron and manganese are separated by filtration, the latter are washed and added to the first portion containing oxide of iron, dissolved in hydrochloric acid, and treated as in No. 25.

From the solution which contains the alkalies, magnesia, and lime, the latter are precipitated by adding a small excess of oxalate of ammonia, the liquid filtered, concentrated by evaporation, and the magnesia precipitated and also washed by a mixture of caustic and carbonate of ammonia. The filtered solution is evaporated to dryness, the mass heated to decompose the nitrate of ammonia, and the alkaline nitrates treated with a mixture of equal parts of alcohol and ether, in which the nitrate of lithia dissolves. The mixture of nitrates of potassa and soda are heated with chloride of ammonium to convert them into chloride, and then separated by chloride of platinum.

The lithia may be separated from both the other alkalies by precipitating as $3\,LiO, PO_5$. The solution is mixed with phosphate of soda, and evaporated to dryness, being kept slightly alkaline, by the addition from time to time of pure caustic soda. The mass is then dissolved in the smallest possible quantity of water, mixed with an equal quantity of ammonia, allowed to stand for twelve hours, filtered, and the precipitate carefully washed with ammonia. If the filtrate is evaporated to dryness, some lithia-salt separates.

Magnesia may also be separated from lithia by adding hot saturated baryta-water to a solution of the chlorides. The lithia is then converted into a sulphate, and as such weighed.

In order to obtain the lithia, the coarsely-powdered mineral is dissolved in concentrated hydrochloric acid, with gradual addition of nitric acid; the solution is heated, to insure the conversion of all protoxide of iron into sesquioxide, and poured off from any extraneous minerals which generally remain undissolved. It is then evaporated completely to dryness, being constantly stirred towards the last, and the mass heated until all free acid is evaporated. It is then finely powdered, boiled out with water, and the solution filtered. This now contains not a trace of iron, which remains undissolved as white phosphate, but only chloride of lithium, mixed with the chlorides of manganese, magnesium, and sodium. In order to precipitate the two former, together with a small quantity of phosphoric acid which may be present, the solution is mixed with pure hydrate of lime, and boiled, with access of air until all the hydrate of protoxide of manganese is converted into the brown sesquioxide. All the lithia remains in the solution; it is filtered off, and the dissolved lime precipitated by a mixture of carbonate of ammonia and free ammonia. After filtration, the solution is evaporated, and the chloride of lithium heated to fusion in a porcelain crucible.

The chloride of lithium still contains chloride of sodium, which is separated by digesting the mass with a mixture of alcohol and ether, which dissolves the chloride of lithium, and leaves the chloride of sodium undissolved. Or the impure chloride of lithium may be converted into carbonate by dissolving it in the smallest possible quantity of concentrated ammonia, and placing in the solution, which should be kept as cold as possible, fragments of carbonate of ammonia. The precipitated carbonate of lithia is filtered off and washed with alcohol.

Pure chloride of lithium is easily fusible; it imparts to the flame of alcohol a dark carmine-red color; when soda is present, the color is rather orange-red.

The Triphylite contains more than 7 per cent. of lithium and more than 44 per cent. of phosphoric acid.

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91. TITANITE (SPHENE).

$(CaO + TiO_2) SiO_2$.

This mineral, even in the state of very fine powder, is only attacked with difficulty, and at best incompletely, by hydrochloric or sulphuric acid.

It is better to heat it in a platinum capsule with bisulphate of ammonia, gradually raising the temperature, with constant stirring, till the salt fuses; the heat is finally increased to ignition. A little dilute sulphuric acid is then added, and heat again applied until the acid begins to volatilize. When the mass is perfectly cold, it is mixed with water, the silicic acid filtered off, and the sulphate of lime thoroughly washed.

From the solution, the titanic acid is precipitated in the cold, together with the small quantity of sesquioxide of iron, by ammonia, the solution filtered rapidly, with as little exposure to air as possible, and the lime precipitated by oxalate of ammonia.

The titanic acid containing iron is dissolved in hydrochloric acid, the solution diluted and carefully neutralized as completely as possible, decomposed by hyposulphite of soda, and heated to ebullition. The titanic acid is precipitated and ignited.

Another method (in which, however, the silicic acid is determined by loss) consists in decomposing the mineral by concentrated hydrofluoric acid. The mass is afterwards mixed with concentrated sulphuric acid, heated until all the tetrafluoride of silicon and most of the sulphuric acid are expelled, mixed once more with concentrated sulphuric acid, and heated until it begins to evaporate. The whole may then be dissolved by adding a sufficient quantity of water.

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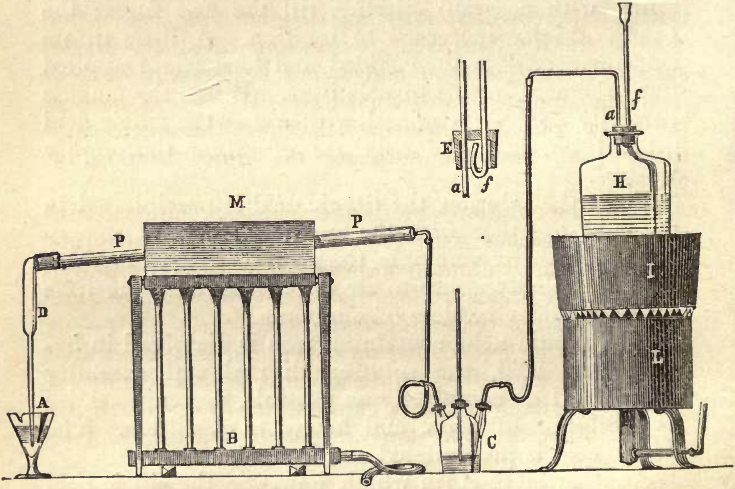
92. MENACCANITE. (TITANIC IRON.*)

$(Ti, Fe)_2 O_3$.

For the analysis of this mineral, and for the preparation of pure titanic acid, various methods are employed. The iron dissolves in concentrated hydrochloric acid but very slowly. When the levigated powder is ignited in hydrogen-gas, the iron is reduced,

Fig. 18.



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* Titanic iron occurs in considerable quantity at Krageröe in Norway, also in fine crystals in Orange Co., N. Y. Most varieties contain magnesia and manganese.

and may be extracted by hydrochloric acid; the reduction, however, requires a very long time and an intense red heat, and, after all, the titanic acid is not free from iron. The following methods are more efficient:—

I. The very finely-powdered mineral is fused in a platinum crucible, placed within an earthen crucible, with 3 parts of carbonate of potassa; the fused mass is powdered, and dissolved in a platinum capsule, in the requisite quantity of dilute hydrofluoric acid. Titano-fluoride of potassium is thus produced, which is sparingly soluble, and crystallizes readily, while most of the sesquioxide of iron is separated free from titanium. The mixture is heated to boiling, so much water being added as is requisite to dissolve all the salt, and filtered while boiling hot; glass vessels may now be employed, provided an unnecessary excess of hydrofluoric acid has been avoided. On cooling, the greater part of the salt separates in lustrous crystalline scales. It is filtered off, pressed, washed once or twice with cold water, and purified completely by recrystallization from boiling water.

The sesquioxide of iron is washed, the washings mixed with the mother-liquor from the salt, and with the washings from the latter, and the dissolved sesquioxide of iron, together with very little titanic acid, precipitated from the mixed solution, in the cold, by dilute ammonia. The precipitate must be filtered off immediately, for otherwise the titanic acid also begins to separate. The filtrate is then heated to ebullition, when all the titanic acid is precipitated as white titanate of ammonia. In the same manner the titanic acid may be obtained from the crystallized titanofluoride of potassium previously separated.

The titanate of ammonia is easily soluble in hydrochloric acid, and, at a red heat, is converted, with incandescence, into pure titanic acid.

II. The finely-powdered mineral is fused with at least 6 parts of bisulphate of potassa in a platinum crucible, until it is completely dissolved; the fused mass, when cool, is powdered and dissolved in cold water.

This solution has the peculiarity, when long boiled, of depositing the whole of the titanic acid, which is not, however, quite free from iron.

In order to obtain it perfectly free from the latter metal, the sesquioxide of iron and titanic acid are precipitated by ammonia, the clear solution decanted from the precipitate, and the latter treated with an excess of sulphide of ammonium, which converts all the iron into black sulphide. After standing for several hours, the mixture is diluted with water, the clear liquor decanted, and the precipitate washed once or twice by decantation.

It is afterwards mixed with sulphurous acid, when it immediately becomes white, since the sulphide of iron dissolves in the form of dithionate of protoxide of iron. The titanic acid is filtered off, washed and ignited, a fragment of carbonate of ammonia being held in the crucible to expel any sulphuric acid.

A little more titanic acid separates from the filtrate on standing for some time, and on gently heating. The iron, when converted into sesquichloride by chlorine, or by heating with hydrochloric acid and chlorate of potassa, may be precipitated from the solution of ammonia.

III. The most accurate method of separation of sesquioxide of iron from titanic acid consists in decomposing the diluted solution from No. II. by hyposulphite of soda. The titanic acid alone is precipitated, which is then ignited.

93. RUTILE.*

TiO_2.

In order to obtain pure titanic acid from rutile, the same method may be employed as for titanic iron; the first process is especially applicable to this purpose.

Or the very finely-powdered rutile is fused in a platinum crucible with six times its weight of bisulphate of potassa. The mass must then dissolve completely in cold water. If the water is heated to ebullition the titanic separates, and by long continued boiling the precipitation is complete. Thus obtained it is nearly soluble in the acids.

Another process consists in converting the titanic acid into bichloride. The very finely-powdered rutile is mixed with ignited lamp-black (1½ part of carbon for 5 parts of rutile) and so much starch-paste as will suffice to form a plastic mass. This is moulded into cylinders about 1 or 2 inches long, and ⅓ of an inch thick, which are slowly dried. They are then thoroughly ignited in a covered crucible, and, while hot, before they have absorbed any moisture, introduced into a tube of porcelain or of hard glass. A stream of dry chlorine is passed in at one end of the tube, while the other opens into a cooled receiver furnished with an egress-tube. As soon as the apparatus is filled with chlorine, the tube is heated to bright redness, and the separation carried on till no more drops of bichloride of titanium distil over. The carbonic oxide and excess of chlorine are passed into a small quantity of alcohol, which absorbs the latter.

The bichloride of titanium, which has a brown color due to sesquichloride of iron, is poured into a small tubulated retort containing some mercury or bright copper-turnings; the neck of the retort is drawn out to a point, which is bent downwards. When the bichloride of titanium has been left for some time in contact with the metal, it is distilled off by gentle ebullition, and immediately received in tubes, which are afterwards hermetically sealed.

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* Occurs most abundantly at St. Yrieix, in France, and may be purchased very reasonably.

In order to prepare pure titanic acid from the bichloride, it is gradually mixed with water, avoiding all rise of temperature, which would render the solution turbid, and the titanic acid precipitated by ammonia.

Pure ignited titanic acid is white, frequently with a tinge of yellow. During ignition it has a lemon-yellow color. When exposed to a very high degree of heat it becomes brownish. It is then perfectly insoluble in hydrochloric acid. By long digestion with concentrated sulphuric acid, it is dissolved.

94. COLUMBITE. (NIOBITE.)*

$(FeO, MnO)(CbO_5\,TaO_5.)$

The mineral is not decomposed by acids. It is best decomposed by fusing it in the form of a levigated powder, with 6 parts of bisulphate of potassa, in a platinum crucible. The salt is first fused by itself, allowed to solidify, the powdered mineral thrown upon it, and the two gradually fused together. The fusion is continued until the mineral has entirely dissolved.

The mass is afterwards repeatedly boiled with water, and the undissolved hydrated acids filtered off and washed. It still contians sesquioxide of iron, and commonly also a small quantity of binoxide of tin and tungstic acid.

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[*] Sp. gr. = 5.4 to 6.39. Often contains small quantities of SnO_2, WO_3 and CaO.

The acids are now digested with sulphide of ammonium, which dissolves the two latter and converts the sesquioxide of iron into sulphide, which imparts a black color to the acids. This may be effected upon the filter itself, if the stem of the funnel be passed air-tight into a flask; the funnel should be kept as closely covered as possible after the mass upon the filter has been carefully mixed with sulphide of ammonium.*

After washing, very dilute hydrochloric acid is allowed to flow over the mass upon the filter, when the sulphide of iron is dissolved, and the acids again become white. They are then washed, dried, and ignited, when the sulphuric acid with which they are combined is volatilized, which may be effected with greater rapidity and certainty if a fragment of carbonate of ammonia be held in the closed crucible during ignition.

The stannic and tungstic acids may be separated with more certainty by fusing the columbic and tantalic acids with three times their weight of alkaline carbonates and sulphur, leached, washed with sulphide of ammonium, and treated as above.

95. TANTALITE.

$(FeO, MnO) TaO_5$.

The analysis is made in the same manner as that of columbite.

The *tantalic acid*, TaO_5, is white, even at a red heat, sp. gr. 7.9. Heated to redness it becomes insoluble in concentrated hydrochloric and sulphuric acids. Fused with caustic potassa or soda, it behaves like niobic acid. The soda-salt may be crystallized. In a solution of this salt it may be precipitated by acids; for example, sulphuric. If precipitated by hydrochloric acid, it is soluble in an excess, although not wholly. With zinc it gives a pale blue color, which becomes very bright if the solution of the bichloride of tantalum in sulphuric acid is mixed with a little water and zinc placed in it. The blue color does not change to brown. Fused with salt of phosphorus it remains colorless in the inner flame, and also when ignited in hydrogen gas.

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* Tin and tungsten may be precipitated by dilute sulphuric acid as sulphides, which are converted in oxides by roasting. If the mass is ignited in hydrogen, the reduced zinc may be extracted by concentrated hydrochloric acid.

The *chloride* of *tantalum*, prepared in the same manner as chloride of columbium, is pure yellow, easily fused, volatile, forms a crystalline sublimate. Water transforms it into hydrated tantalic acid and hydrochloric acid, which does not retain it in solution.

If the tantalic acid contains titanic acid, by converting it into the chloride, a very fuming liquid bichloride of titanium is formed. By fusion with bisulphate of potassa the separation is incomplete.

96. WOLFRAMITE.

$(MnO, FeO), WO_3$.

I. In order to effect merely a qualitative separation, for obtaining tungstic acid, the very finely-powdered mineral is digested with a mixture of concentrated hydrochloric acid and about ¼ of nitric acid, until it is converted into yellow, pulverulent tungstic acid. This is filtered off, washed, dissolved in ammonia,* the solution filtered, and evaporated to crystallization. On igniting the salt in the air, pure yellow tungstic acid is left.

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* By this treatment, there is left undissolved, besides the undecomposed particles of mineral which have not been finely powered, a white substance, consisting of silica and niobic acid, of which latter the wolfram contains about 2 per cent. In order to remove the silica, it is repeatedly evaporated with hydrofluoric and sulphuric acids, then fused with bisulphate of potassa and farther treated as directed for columbite.

Or 3 parts of the mineral, very finely powdered, may be mixed with an equal quantity of carbonate of potassa, or $\frac{2}{3}$ dry carbonate of soda, the mixture heated to redness for half an hour, and the tungstate of potassa which is formed, may be extracted from the cooled mass with water.*

Pure tungstic acid may be obtained from this solution by boiling, and adding drop by drop hydrochloric acid or nitric acid, not too dilute, until there is a small excess. From the solution neutralized with hydrochloric acid, tungstate of lime may be precipitated by chloride of calcium which may be decomposed, after washing, by boiling hydrochloric acid.

If very finely-powdered tungsten, with an excess of chloride of calcium, is kept in a state of fusion for some time, and the cooled mass dissolved in water, small brilliant octahedral crystals of tungstate of lime are obtained.

If tungstic acid is gently ignited in a stream of hydrogen, a blue tungstate of the oxide of tungsten is formed, with a stronger heat, brown oxide, and a still higher temperature, metallic tungsten as a gray crystalline powder.

II. For quantitative analysis, the levigated mineral is digested with a mixture of 4 parts of concentrated hydrochloric acid and 1 part of nitric acid, until it is completely decomposed; the solution is then evaporated to dryness, which operation should be finished on the water-bath, the chloride of manganese and sesquichloride of iron dissolved out, the tungstic acid filtered off, washed with alcohol, dissolved in ammonia, separated by filtration from the columbic acid, the solution evaporated, the residual ammonia-salt ignited with access of air, and the tungstic acid weighed.

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* If the solution is green from the presence of a manganate, it may be decomposed by adding a little ammonia and warming. On dissolving the residual proto-sesquioxides of iron and manganese or the metallic sulphides obtained as above mentioned in concentrated hydrochloric acid, columbic acid remains behind.

The filtrate, containing alcohol, is evaporated to expel the latter, diluted with water, and the oxides of manganese and iron separate as in No. 25. They usually contain a little lime.

Or the levigated mineral is ignited in a platinum crucible, with 3 parts of carbonate of potassa, the mass dissolved in water, the residual oxides thoroughly washed, the solution neutralized with nitric acid, and the tungstic acid precipitated by nitrate of suboxide of mercury, the free nitric acid being afterwards neutralized with a few drops of ammonia, so that a black precipitate begins to appear. The precipitate is thoroughly washed, a very dilute solution of nitrate of suboxide of mercury being used at last, since otherwise, the precipitate is liable to pass through the filter; it is then dried and ignited, when pure tungstic acid is left.

Or the solution of alkaline tungstates is neutralized with nitric acid, the tungstic acid precipitated by acetate of lead, with addition of a few drops of ammonia. The washed precipitate is decomposed by digestion with sulphide of ammonium, which dissolves all the tungsten as a sulphide. The filtrate from the sulphide of lead is evaporated to dryness, the mass carefully oxidized with nitric acid, and again evaporated to dryness and ignited.

The mixture of the oxides of iron and manganese is dissolved in concentrated hydrochloric acid, which usually leaves undissolved a small quantity of tungstic, columbic, and silicic acids. The two oxides are then separated as in No. 25.

97. SCHEELITE.

CaO, WO_3.

The mineral, very finely powdered, is digested with concentrated nitric acid, the mass evaporated nearly to dryness, mixed with alcohol, and filtered. The residual yellow tungstic acid is washed with alcohol, ignited and weighed. The alcohol is expelled from the solution by evaporation, the latter neutralized with ammonia, and the lime precipitated by oxalate of ammonia.

98. WULFENITE (MOLYBDATE OF LEAD).

PbO, MoO_3.

Several methods are employed for obtaining the molybdic acid from this mineral.

I. In order to remove the carbonates of zinc and of protoxide of iron, the finely-powdered ore is treated for some time, and frequently agitated, with dilute hydrochloric acid; it is afterwards washed by decantation, and decomposed by boiling concentrated hydrochloric acid. The mixture is then evaporated to dryness, the residue powdered, and digested with ammonia. Insoluble basic chloride of lead and molybdate of ammonia are thus formed; the solution containing the latter is filtered off, and evaporated to crystallization. The mother-liquor from the crystals, or even the entire solution, may be mixed with nitric acid, evaporated to dryness, and the residue extracted with water, when the molybdic acid is left.

II. The powdered ore is fused with an equal weight of dry carbonate of soda, the fused mass poured out, taking care to separate it as far as possible from the oxide of lead which has settled at the bottom, and dissolved in hot water; the small quantity of lead carried into solution is precipitated from the latter, while hot, by a mixture of ammonia and carbonate of ammonia, the solution filtered, acidified with nitric acid, evaporated to dryness, the nitrate of soda extracted from the mass with water, and the molybdic acid thoroughly washed.

III. In order to avoid the perforation of the crucible, which occurs frequently in this process, the ore may be fused with an equal weight of carbonized bitartrate of potassa, when the lead separates in the metallic state, without any reduction of molybdic acid taking place.

IV. The powdered ore is fused with an equal weight of calcined bitartrate of potassa and as much sulphur; the sulphomolybdate of potassa thus produced is dissolved in water, and the sulphide of molybdenum precipitated from the solution by dilute sulphuric acid. When this precipitate is washed, dried and ignited in a covered crucible, it leaves a crystalline gray sulphide, from which molybdic acid may be prepared by the method employed in treating molybdenite.

Also by heating the finely pulverized mineral with caustic soda and sulphur, which converts the molybdic acid into a sulphide, which is then precipitated by an acid as MoS_2. There still remains in solution some molybdenum which may be precipitated by hydrosulphuric acid.

V. The finely powdered mineral is digested, with constant stirring, with $1\frac{1}{4}$ parts of concentrated sulphuric acid, until it is perfectly white. The heat is then raised to incipient volatilization of sulphuric acid the mixture allowed to cool, and the blue pasty mass stirred up with much water, in order to separate the sulphate of lead; the solution containing the molybdic acid is decanted, filtered and evaporated in a porcelain dish with addition of some nitric acid, until the sulpuric acid begins to evaporate; the mixture should be constantly stirred. The molybdic acid is thus separated as a white precipitate; when the greater part of the sulphuric acid has been expelled, the mixture is diluted with water, the molybdic acid filtered off and well washed, water containing nitric acid being used towards the end. Some more molybdic acid may be obtained by evaporating the filtrate and washings. It is free from phosphoric acid.

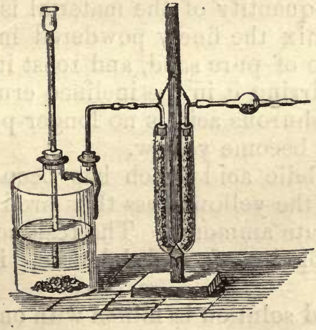
If it contain any phosphoric acid, its ammoniacal solution, when acidified with nitric acid, and heated, becomes yellow and deposits a yellow powder.

The molybdic acid may be obtained from molybdate of ammonia by gradually heating the salt, with free access of air.

It is always obtained in a perfectly pure state by sublimation, for which purpose it is heated in a platinum crucible, which is covered with a platinum capsule kept full of water.

For quantitative analysis, the pure crystallized mineral is finely powdered, completely decomposed by digestion with nitric acid, the mixture neutralized with ammonia, and digested with an excess of sulphide of

Fig. 19.



ammonium. The sulphide of lead which is thus formed, is filtered off from the dissolved molybdate, washed with dilute sulphide of ammonium, dried at 100°, and weighed. From the solution, the sulphide of molybdenum is precipitated by dilute nitric acid, collected upon a filter, dried at 100°, washed, dried, and weighed. A weighed portion of it is then introduced into a bulb-tube (Fig. 19), and heated in a stream of hydrogen until it loses no more sulphur. From the weight of the residual MoS_2, calculated for the total amount of the precipitate, that of the molybdic acid is ascertained.

99. MOLYBDENITE.

MoS_2.

The mineral in small fragments is heated in a tube of hard glass, through which a very slow stream of dry air is passed, forming sulphurous acid and molybdic acid, the latter subliming in colorless needle-shaped crystals.

If a large quantity of the material is to be used, it is better to mix the finely powdered mineral with an equal volume of pure sand, and roast it at a red heat, frequently stirring it in the inclined crucible, until the smell of sulphurous acid is no longer perceptible, and the mass has become yellow.

The molybdic acid which has been formed is extracted from the yellow mass thus produced, by digestion with dilute ammonia. The residue, should it still contain sulphide of molybdenum, is then again roasted.

The filtered solution is mixed with one or two drops of sulphide of ammonium, to separate the copper, the precipitate filtered off, the solution evaporated to dryness, the salt again dissolved in dilute ammonia, the solution filtered from any impurities, and evaporated to crystallization. (*See* Molybdate of Lead.)

The molybdic acid may also be precipitated from the solution of an alkaline molybdate neutralized with nitric acid, by basic nitrate of suboxide of mercury. The yellow precipitate is allowed to subside, filtered off, washed with a dilute solution of the mercury-salt, dried and ignited. Molybdic acid may also be quantitatively determined, by this method. The precipitate is collected upon a filter (previously dried at 100° and weighed), dried at 100°, and a weighed portion of it gently ignited in a bulb-tube (Fig. 19), through which a stream of hydrogen is passed, when dark brown binoxide of molybdenum, MoO_2, is left.

100. BROWN IRON-ORE, CONTAINING VANADIUM.

In order to extract the vanadium, the quantity of which does not amount even to 1 per cent., the finely-powered ore is intimately mixed with $\frac{1}{3}$ its weight of nitre, and exposed, for an hour, in a crucible, to a gentle ignition. When cool, the mass is powdered and boiled with water.

The filtered solution has a yellow color, and contains the vanadates, chromates (molybdates ?), arsenates, phosphates, nitrites and silicates of potassa and alumina.

It is gradually mixed, and well stirred, with nitric acid, taking care that it may still remain slightly alkaline and that no nitrous acid is liberated, which would reduce the vanadic and chromic acids. The precipitate of alumina and silica thus separated is filtered off.

The solution is then mixed with an excess of solution of chloride of barium, as long as any precipitate is produced. The precipitate, consisting of the baryta-salts of the above-mentioned acids, is filtered off, washed and boiled while yet moist, with dilute sulphuric acid, which must not be added in too great excess. The reddish-yellow acid filtrate is neutralized with ammonia, concentrated by evaporation, and a fragment of chloride of ammonium is placed in it. In proportion as the solution becomes saturated with chloride of ammonium, vanadate of ammonia is deposited as a white or yellow crystalline powder, which is allowed to separate completely, filtered off, and washed with a saturated solution of chloride of ammonium. When gradually heated with full access of air, it leaves dark red vanadic acid, which fuses when heated more strongly, and solidifies, on cooling, to a very crystalline mass.

The solution obtained by lixiviating the mass after fusion with nitre, may also be mixed with sal-ammoniac, and boiled, in order to neutralize the free alkali, and to precipitate silica and phosphate of alumina. This precipitate usually contains also vanadic acid, which may be converted into sulphide by fusion with an equal weight of carbonate of potassa and sulphur; the fused mass is extracted with water, and the brown sulphide of vanadium precipitated from the filtered solution by dilute sulphuric acid.

If the iron-ore be reduced by fusion with borax (*see* Iron Assay), in a crucible lined with charcoal, a well-fused, crystalline regulus of iron is obtained, which contains vanadium, chromium, arsenic, phosphorus, silicon, and carbon.

Moreover, *see* Ash of the Refining-hearth.

101. VANADINITE. (VANADATE OF LEAD.)

$PbCl, + 3 (3\,PbO, VO_3)$.

There exist some varieties of this mineral, at present very rare, which contain no chloride of lead.

This mineral, when treated with nitric acid, first becomes red, then dissolves. If the solution be mixed with ammonia, and afterwards with an excess of sulphide of ammonium, sulphide of lead is precipitated, and a dark red solution obtained, from which acids precipitate the dark brown sulphide of vanadium. The precipitate is roasted in air, and afterwards converted into vanadate of potassa by fusion with a small quantity of nitre. This salt is dissolved in a little water, and vanadate of ammonia precipitated from the solution by sal-ammoniac. (*See* No. 100.)

The mineral is only imperfectly decomposed by sulphuric acid. The decomposition, however, is complete if it be fused with bisulphate of potassa. On treating the mass with water, the lead remains behind as sulphate, while vanadic acid is dissolved.

Or the mineral may be decomposed by a mixture of concentrated hydrochloric acid and alcohol, the chloride of lead is washed with alcohol, and the excess of acid evaporated from the blue solution of chloride of vanadium. This solution is treated with an excess of caustic soda, and the oxide of vanadium is converted into vanadic acid by a current of chlorine gas.

102. CHROMITE. (CHROME-IRON-ORE.)

FeO, Cr_2O_3.

I. For the mere qualitative separation, the very finely powdered ore is fused for at least half an hour, at a bright red heat, with an equal weight of nitre and as much carbonate of potassa; from the fused mass, when cool, the chromate of potassa which has been produced is extracted with water.

The residue, consisting of sesquioxide of iron and variable quantities of alumina and magnesia, is dissolved in concentrated hydrochloric acid, which generally leaves some undecomposed mineral, and the three oxides are then separated as in No. 81.

The solution of chromate of potassa usually contains a little alumina, silica and manganic acid, to precipitate which, it is mixed with a little carbonate of ammonia and boiled.

In order to obtain bichromate of potassa from this solution, it is acidified with nitric acid, concentrated by evaporation, and the salt allowed to crystallize out.

The chromic acid may be precipitated as chromate of lead, by neutralizing the solution with acetic acid and adding acetate of lead.

To separate the chromium as sesquioxide, the solution, is acidified with sulphuric acid, sulphurous acid added till the solution has an emerald-green color, the sesquioxide of chromium precipitated by ammonia, washed and ignited.

Or the yellow solution may be exactly neutralized with nitric acid, and the chromic acid precipitated by nitrate of suboxide of mercury. When washed, dried and ignited, the yellowish-red chromate of suboxide of mercury leaves a pure green sesquioxide of chromium.

II. Chromite may also be quantitatively analyzed by the above process, the fusion being conducted in a platinum crucible, though it will be found that a quantity of ore will be left undecomposed, varying according to the state of division to which it was reduced. From the solution, after neutralization with nitric acid, the chromic acid is best precipitated by nitrate of suboxide of mercury; the precipitate is washed with a dilute solution of that salt and ignited. The following method is more certain.

The mineral, which should be powdered as finely as possible and weighed, is fused, in a platinum crucible, with four times its weight of bisulphate of potassa, care being taken that the mass, which froths up at first, may not run over the side of the crucible. Ultimately, it is heated to redness, and retained in fusion, at a red heat, for a considerable time. The salts formed are sparingly soluble in water and acids; the sesquioxide of chromium must therefore be converted into alkaline chromates, for which purpose there is added to the cooled mass, in the crucible, about twice its volume of a mixture of equal parts of nitre and carbonate of soda. The mass is then heated to complete fusion.

On cooling, the chromate of potassa is extracted with hot water, the residue of sesquioxide of iron, alumina and magnesia, thoroughly washed, dissolved in concentrated hydrochloric acid, and analyzed as in No. 81.

The solution of chromate of potassa is acidified with hydrochloric acid, heated to ebullition, and alcohol added to the boiling solution until it has acquired an emerald-green color, when the sesquioxide of chromium is precipitated by ammonia, ignited and weighed.

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103. CHROMATE OF LEAD.

PbO, CrO_3.

(Chrome-yellow, often adulterated with white clay, with BaO, SO_3,—CaO, CO_2,—CaO, SO_3, or with PbO, SO_3.)

I. Pure chromate of lead should give the quantities of oxide of lead and chromic acid calculated from the formula.

For analysis, it is digested with a mixture of fuming hydrochloric acid and alcohol, when a green solution of sesquichloride of chromium is produced, the lead remaining undissolved as a white chloride. The latter is collected upon a filter, dried at 100°, washed with alcohol, and dried at 100°. The solution is diluted with water, evaporated to expel the alcohol, and the sesquioxide of chromium precipitated by ammonia; the liquid is heated to ebullition, the precipitate filtered off, ignited and weighed.

II. For mere qualitative analysis of a specimen of chrome-yellow mixed with the substances mentioned above, it is treated as before, with alcohol and hydrochloric acid, as little as possible of the latter being employed, in order that the clay may remain untouched.

From the solution, the sesquioxide of chromium is precipitated by ammonia; it always, however, carries down some lime.

In order to separate them accurately, they must be precipitated together, from the hot solution, by a mixture of ammonia and carbonate of ammonia. After drying, the precipitate is fused with three times its weight of a mixture of carbonate and nitrate of potassa, and the fused mass treated with water, which dissolves the chromate of potassa, and leaves the carbonate of lime.

Or the precipitate, while yet moist, may be digested with hypochlorite of soda, which dissolves the sesquioxide of chromium, as chromate of soda, leaving the carbonate of lime undissolved. The solution is then heated to ebullition, in order to decompose any bicarbonate.

From the residue, which may consist of the sulphates of lime, baryta, and lead, the first may be entirely extracted by washing with water, or with a solution of common salt or of sal-ammoniac, in which it is far more soluble. In the solution, either the sulphuric acid is precipitated, by a baryta-salt, or the lime by an oxalate.

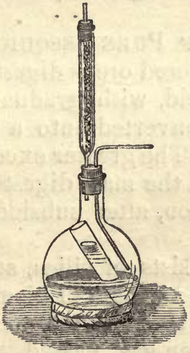
The sulphate of lead is extracted from the residue by digestion with tartrate of ammonia containing free ammonia, and the lead precipitated from the solution by sulphuretted hydrogen or chromate of potassa.

The mixture of clay and sulphate of baryta which remains at last, is heated with concentrated sulphuric acid until the greater excess of the latter has been expelled, when the sulphate of alumina is extracted with water, and the alumina precipitated by ammonia.

In order to extract the silica from the residue, which contains also sulphate of baryta, it is boiled in a concentrated solution of carbonate of soda, in which the silica is dissolved and may be reprecipitated by sal-ammoniac. The residue consists of carbonate of baryta mixed with more or less undecomposed sulphate of baryta. (*See* No. 15.)

A good method of determining the amount of chromic acid (and therefore of chromate of lead contained in a specimen of commercial chrome-yellow,

Fig. 20.



consists in reducing the chromic acid to the state of sesquioxide of chromium by means of oxalic acid, and in determining the quantity of carbonic acid produced.

This may be effected in the same way as the testing of manganese-ores in an apparatus (Fig. 20) arranged for the quantitative determination of carbonic acid, the weighed chromate of lead being mixed with oxalate of potassa, and sulphuric acid allowed to flow upon it. 10 parts by weight of carbonic acid indicate 7.6 parts of chromic acid, or 24.5 of pure chromate of lead. Hence, 100 parts of pure chrome-yellow should give 40.4 of carbonic acid.

104. URANINITE.

$UO, U_2O_3,$

(together with various extraneous substances, in variable quantities, including silica, iron, nickel, cobalt, zinc, copper, bismuth, lead, manganese, arsenic, antimony, sulphur, lime, and manganese; sometimes also selenium and vanadium).

PREPARATION OF PURE SESQUIOXIDE OF URANIUM.—The finely-powdered ore is digested with moderately dilute sulphuric acid, with gradual addition of nitric acid, until it is converted into a white powder, and partly dissolved. The greater excess of sulphuric acid is then evaporated, the mass digested with much water, and the cold solution, after subsidence of the residue, filtered off.

The residue consists of silica, sulphate of lead and basic sulphate and arsenate of bismuth.

The solution is then heated to about 60°, and sulphuretted hydrogen-gas passed through it, at this temperature, for some time; the solution is afterwards allowed to cool while the gas is still passing, and, when fully saturated, set aside in a covered vessel for twenty-four hours. The sulphuretted hydrogen is then expelled by a gentle heat, and the precipitate filtered off.

The precipitate contains arsenic, antimony, copper, and the rest of the lead and bismuth.

The solution is then heated to ebullition, and fuming nitric acid gradually added to the boiling liquid, until all the protoxide of iron is reconverted into sesquioxide, and the solution has acquired a pure yellow color. It is then precipitated by an excess of ammonia, and the yellowish-brown precipitate filtered off.

Part of the nickel, cobalt, zinc, lime and magnesia remain in solution, but the remainder is precipitated together with the sesquioxides of uranium and iron.

The washed precipitate is treated with a hot, pretty strong solution of carbonate of ammonia containing free ammonia, with which the precipitate is digested, at a moderate heat, until it has the appearance of hydrated sesquioxide of iron. The solution of uranium is rapidly filtered off, while hot, and the residue of hydrated sesquioxide of iron (still containing uranium) is washed, the washings being received apart from the filtrate.

The solution (which is yellow, or colored reddish by the cobalt) deposits on cooling, if sufficiently concentrated, crystals of the pure double carbonate of ammonia and sesquioxide of uranium, which may be collected, and washed several times with cold water. When ignited, this salt leaves pure dark green proto-sesquioxide of uranium.

The mother-liquor is mixed with the washings and sulphide of ammonium carefully added, drop by drop, as long as it produces a dark brown precipitate, which is immediately filtered off.

The precipitate consists of the sulphides of cobalt, nickel and zinc.

The yellow filtrate is then boiled till the greater part of ammoniacal salt is volatilized, and all the sesquioxide of uranium precipitated.

The pure yellow precipitate, uranate of ammonia is filtered off, and, when the filtrate begins to pass through turbid, washed with solution of sal-ammoniac.

When ignited, it leaves dark green proto-sesquioxide of uranium. By digesting this with dilute hydrochloric acid, any lime and magnesia may be extracted.

In order to prepare protoxide of uranium from the uranate of ammonia, it is dissolved in hydrochloric acid, the solution mixed with an excess of pure sal-ammoniac, and about an equal quantity of pure common salt; it is then evaporated to dryness, and the mass heated in a covered crucible until the sal-ammoniac is volatilized, and lastly, until the common salt fuses. On dissolving it in water, the protoxide of uranium is left as a heavy crystalline powder. The common salt only serves to shield the oxide from the action of air.

When the quantity is very small, the uranate of ammonia is calcined and the proto-sesquioxide is dissolved in hydrochloric acid with a few drops of nitric acid; the addition of chloride of potassium forms a substance $U_2 O_2 Cl + R Cl$. It is evaporated to dryness and the yellow salt ignited in a current of hydrogen.

In order to extract from the hydrated sesquioxide of iron the small quantity of sesquioxide of uranium which is chemically combined with it, it is dissolved in the smallest possible quantity of hydrochloric acid, the solution neutralized with carbonate of ammonia, and added, drop by drop, with constant stirring, to a mixture of carbonate of ammonia and sulphide of ammonium, when all the iron is separated as sulphide, and the sesquioxide of uranium remains in solution; the latter may be precipitated by boiling the filtrate.

Or the sesquioxide of iron may be reduced in a stream of hydrogen, and the reduced pyrophoric mass allowed to fall, immediately, into dilute hydrochloric acid, which dissolves the iron, leaving the uranium a protoxide.

In order to detect selenium, arsenic, and vanadium in pitch-blende, it is ignited with ¼ of its weight of a mixture of carbonate of soda and nitre. The selenates, vanadates and arsenates of the alkalies may then be extracted with water.

105. SELENIFEROUS DEPOSIT FROM SULPHURIC ACID CHAMBERS.

(Sulphate of lead, selenium, selenide of mercury, selenates selenites, &c.)

The dry mass is rubbed to a thin paste with a mixture of about equal parts of sulphuric acid and water, and boiled for a long time, concentrated nitric acid or chlorate of potassa being added at intervals, to oxidize the free selenium, until all the reddish color has disappeared.

The mixture is then diluted with water and filtered. The solution contains, besides iron, copper, mercury and a little lead, all the selenium as selenious and selenic acids. It is mixed either with about as much common salt as amounts to half the weight of the deposit originally employed, or with ¼ of its volume crude of fuming hydrochloric acid, and boiled down to about ¼ of its original bulk. The hydrochloric acid reduces the selenic acid to selenious acid.

On cooling, the solution is poured off from any sulphate of potassa and common salt which may have been deposited; these are washed several times with water, and the solution saturated with sulphurous acid gas, evolved from a mixture of powdered charcoal and concentrated sulphuric acid.

The selenium is thus precipitated of a fine red color. Its separation is promoted by digestion, and ultimately by boiling for a quarter of an hour, when it becomes black, and collects into a dense hard mass. It is well washed and dried.

The filtered liquid is boiled once more with hydrochloric acid, and again treated with sulphurous acid, in case it should still contain selenium.

The selenium thus obtained contains still small quantities of lead, copper, and iron, and especially mercury. On distilling it in a small retort or bent tube closed at one end, the first-mentioned impurities are left behind as selenides.

In order to free it from mercury, the distilled selenium is dissolved in *aqua-regia*, the greater excess of acid evaporated, so that no nitric acid may remain, the solution mixed with excess of carbonate of soda, evaporated to dryness, and the saline mass ignited to expel the mercury.

The mass is redissolved in water, the solution boiled with hydrochloric acid, and the selenium again precipitated by sulphurous acid.

Or the ignited mass may be mixed with about an equal weight of chloride of ammonium, and heated in a retort till the greater part of that salt has sublimed, when the selenium is reduced, and remains behind on dissolving the saline mass in water.

The selenium may also be at once extracted, and obtained free from mercury, by fusing the deposit, with an equal weight of carbonate of soda and about ¼ of nitre, in a crucible. When the mass is in a state of tranquil fusion, it is poured out, so as to leave the oxide of lead, as far as possible, at the bottom of the crucible. It is then dissolved in water, the solution acidulated with sulphuric acid, the precipitated sulphate of lead filtered off, and the filtrate treated, as above, with hydrochloric acid and sulphurous acid.

It is necessary in this process that all the nitric acid from the nitre should either be expelled or decomposed, for otherwise part of the selenium will escape precipitation.

Or the solution of the fused saline mass is saturated with hydrochloric acid, chloride of ammonium added, evaporated to dryness, and the mass heated in a retort until the chloride of ammonium begins to sublime, when all the selenium is reduced.

106. SELENIUM SOOT.*

(Selenium with Selenides, Coal, Sand, &c.)

The black mass is moistened with sulphuric acid, thoroughly washed, fully dried and distilled from a porcelain or hard glass retort, with a strong heat, until most of the selenium passed over nearly pure.

The residue consisting of selenides, coal and other impurities, is dissolved in hydrochloric acid with gradual addition of nitric acid, and while hot the copper and iron are precipitated by caustic soda, the solution filtered, and the selenium precipitated by saturating with sulphurous acid, or reduced by adding an excess of chloride of ammonium, evaporating to dryness and heating until the chloride of ammonium begins to sublime, when the alkaline salt is washed out. If the selenium is precipitated directly from the solution containing copper more or less of this metal is thrown down.

In order to detect and separate the sulphur in the selenium, it is dissolved in very strong nitric acid, the solution mixed with hydrochloric acid, heated for some time to boiling, and the sulphuric acid precipitated by chloride of barium. The excess of baryta in the filtered solution is then precipitated by sulphuric acid, and afterwards the selenium by sulphurous acid.

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* It collects in the chimneys where the copper ores are roasted at Mansfeld. It contains from 30 to 40 per cent. of selenium after it is washed and dried.

In order to prepare selenious acid, the selenium is dissolved in nitric acid, carefully evaporated to dryness, and the acid sublimed in a retort.

To prepare selenic acid, the selenious acid is saturated with pure carbonate of copper and chlorine passed into it until all the selenious salt is dissolved. The solution is then again saturated with carbonate of copper, concentrated by evaporation, and the selenate of copper precipitated by alcohol, the chloride of copper remaining in solution. The precipitate is first washed with alcohol, then dissolved in water and the copper precipitated by sulphuretted hydrogen.

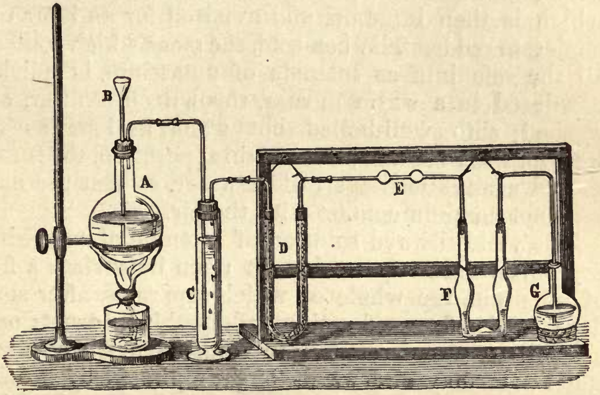
107. CLAUSTHALITE. (SELENIDE OF LEAD.)

$PbSe$.

The analysis is best effected, like that of tetrahedrite (No. 63), by means of chlorine-gas (Fig. 21). After the decomposition, the bulb is again weighed, in order to ascertain the amount of lead present. The greater part of the selenium is volatilized in the form of the solid chloride; only a small quantity of the liquid chloride passes over at first. These are conducted into water, which is afterwards saturated with chlorine, in order to convert all the selenious acid into selenic acid; the latter is then precipitated by chloride of barium, and the selenium determined as selenate of baryta; 100 parts of the latter correspond to 28.2 of selenium.

If the metallic selenides are mixed or combined with the metallic sulphides, as, for example, in the native selenide of mercury which contains sulphide of mercury, the sulphuric acid and selenic acid formed in the analysis are precipitated together by chloride of barium, the precipitate ignited and weighed. A weighed quantity is then heated in a bulb-tube, through which a stream of dry hydrogen is passed, when the selenate of baryta is reduced, with great facility, to the state of selenide of barium, while the sulphate of baryta remains unaltered. The selenide of barium is then extracted with dilute hydrochloric acid.

Fig. 21.



In the same way the other metallic selenides which occur as minerals may be analyzed, viz., the selenide of silver and lead, the selenide of cobalt and lead, and the selenide of mercury and lead.

In order to obtain the selenium from the selenide of lead occurring in many places in the Hartz, the mineral is powdered, treated with dilute hydrochloric acid to remove the calcareous spar and spathic iron-ore, well washed and dried. It is then very intimately mixed with an equal weight of carbonate of potassa containing charcoal (calcined bitartrate of potassa), covered with coarse charcoal-powder in a crucible, the cover of which is then luted on, and exposed for an hour to a moderate red heat. When cool, the mass, which contains all the selenium as selenide of potassium, is quickly powdered in a warm mortar, thrown on a filter, and washed with well-boiled hot water, as long as the washings are colored; during this operation, the funnel should always be kept full of water, so that the mass may not come in contact with the air.

The yellowish-red solution of selenide of potassium begins immediately to deposit upon its surface a film of selenium, the whole of which separates, after some days, in the form of a thin reddish-black crust; only a small quantity remains in solution in an oxidized state. It may afterwards be precipitated by heating the solution with sulphurous and hydrochloric acids.

Since selenide of lead frequently contains selenide of silver, the carbonaceous mass remaining after the extraction of the selenide of potassium may be fused with carbonate of potassa and some nitre. A metallic button of argentiferous lead is thus obtained, from which the silver may best be separated by cupellation.

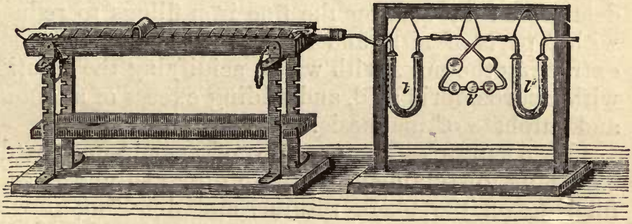
108. CAST-IRON.

For the detection and estimation of the foreign substances, the total weight of which does not usually exceed 5 per cent., it is best to employ separate portions of iron.

I. CARBON.—The total amount of carbon may be determined by burning the iron, in the state of very fine filings, with the aid of a slow stream of pure oxygen, as in organic analysis; the carbonic acid which is produced being collected in a weighed potash bulb (Fig. 22).

The whole amount of carbon may be determined more accurately by dissolving the iron in water, with 5 parts of iodine. The residue is filtered through asbestos and afterwards ignited in a current of oxygen gas. Or it may be heated in a proper apparatus with six times its weight of bichromate of potassa and an excess of moderately concentrated sulphuric acid, when all the carbon is converted into carbonic acid. The iron may be treated at once in a similar manner.

Fig. 22.



Another quantity of the iron-filings is dissolved in dilute sulphuric acid, when the combined carbon is evolved in combination with hydrogen, while the graphite is left undissolved. In this operation, the gas may be conducted through a solution of acetate of lead, when the presence of sulphur is indicated by the precipitation of sulphide of lead.

The residue insoluble in the acid is well washed, dried at 200°, and burnt, as above, in oxygen-gas. From the amount of carbonic acid, that of the graphite is calculated.

II. Silicon.—The residue from the first carbon-determination, which contains all the silicon in the form of silicic acid, is dissolved in concentrated hydrochloric acid, the solution evaporated to dryness on the water-bath, the mass digested with dilute hydrochloric acid, and the silicic acid filtered off.

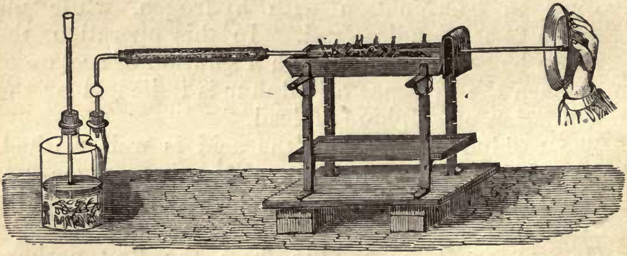
III. PHOSPHORUS.—From the solution filtered from the silica, the phosphoric acid is separated as in No. 22. If the iron contain arsenic, it is obtained as arsenic acid, together with the phosphoric acid.

Or a larger quantity of iron is dissolved in *aqua-regia*, precipitated with ammonia, filtered, dried without washing, mixed with about an equal portion of carbonate of soda, heated to redness for half an hour, the mass completely dissolved in water, the solution concentrated and the phosphoric acid precipitated as in No. 9.

The amount of phosphorus may be less accurately determined by heating the fine iron-filings to redness with 2 parts of nitre and 1 part of carbonate of soda, extracting the mass with water, acidifying the solution with hydrochloric acid, and adding excess of ammonia and sulphate of magnesia.

IV. ARSENIC.—The presence of arsenic may be detected by dissolving the iron in dilute sulphuric acid, filtering off the black residue, and digesting it with sulphide of ammonium. From the filtered solution dilute sulphuric acid precipitates the pentasulphide of arsenic. The precipitate is dissolved in *aqua-regia*, the

Fig. 23.



nitric acid expelled by evaporation, and the arsenic reduced in Marsh's apparatus.

The solution of iron filtered from the black residue is neutralized with carbonate of soda, mixed with a few drops of sesquichloride of iron, and then with acetate of soda, when arseniate of sesquioxide of iron is precipitated, may be easily decomposed by sulphide of ammonium.

For the quantitative determination of the arsenic, the cast-iron is dissolved in hydrochloric acid, with gradual addition of nitric acid, the solution filtered from the carbon, and heated with sulphurous acid till all the sesquichloride of iron is converted into protochloride; the excess of sulphurous acid is then expelled by heat, and the solution saturated with sulphuretted hydrogen, and allowed to stand for twenty-four hours in a closed vessel; the excess of gas is afterwards evaporated, and the precipitate filtered off.

V. COPPER.—This metal is contained in the precipitate produced as above, by sulphuretted hydrogen. After drying, it is distilled in a tube, when sulphide of copper remains behind. Or the sulphide of arsenic may be dissolved out by solution of potassa, or more completely, by solution of monosulphide of potassium.

VI. MANGANESE.—The solution filtered from the precipitate produced by sulphuretted hydrogen, in V. is heated to the boiling-point, and the protoxide of iron entirely converted into sesquioxide by adding chlorate of potassa or hydrochlorite of soda. The oxide of manganese and sesquioxide of iron are then separated from each other by means of bicarbonate of soda, as in No. 25.

VII. ALUMINUM.—The alumina is contained in the sesquioxide of iron which is then precipitated and may be separated from it as in No. 21.

VIII. MAGNESIUM AND CALCIUM remain, together with the protoxide of manganese, in the solution filtered from the precipitate produced by bicarbonate of soda. (*See* No. 25.)

IX. CHROMIUM AND VANADIUM.— A large quantity of the iron-filings is ignited with 2 parts of nitre and 1 part of carbonate of soda, the mass extracted with water, and the solution treated as in No. 100, when phosphoric and arsenic acids may likewise be sought. It is safer to employ for this purpose the carbonaceous residue obtained by dissolving a large quantity of the iron in dilute sulphuric acid.

X. MOLYBDENUM.—Sometimes this metal is extracted, together with the arsenic, by sulphide of ammonium, from the black carbonaceous residue; in such a case, it is reprecipitated, together with the pentasulphide of arsenic, an adding an acid to the solution. If this precipitate be distilled in a tube, the sulphide of molybdenum is left behind.

If the cast-iron is rich in molybdenum, it is dissolved in *aqua-regia* and the molybdenum precipitated by hydrosulphuric acid, placing in the acid solution at the same time a piece of zinc, which renders the precipitation complete.

XI. SULPHUR.—The sulphur may be determined approximately by evolving it as sulphuretted hydrogen, as in No. 1, when the iron is dissolved in dilute sulphuric acid. Or it exists as sulphuric acid in the solutions obtained at III. and VI., and may be precipitated by chloride of barium. Or a large quantity of iron may be dissolved in *aqua-regia*, and the sulphuric acid formed may be precipitated from the diluted solution by chloride of barium.

XII. NICKEL AND COBALT may be detected in the solution from which the copper has been removed by sulphuretted hydrogen. This solution is r-eoxidized, and the sesquioxide of iron precipitated by carbonate of baryta, after which the nickel and cobalt are precipitated by sulphide of ammonium.

For the detection of most of the admixtures, it is best to employ the black residue which is left on dissolving the iron in dilute sulphuric acid, and which can easily be prepared in considerable quantity. It contains silicic acid, carbon, carbide of iron, phosphide of iron, arsenide of iron, compounds of chromium and vanadium with iron, molybdenum, &c.

The total amount of the carbon (phosphorus, arsenic, chromium, &c.?) in iron may be separated by digesting the fine iron-filings with a solution of chloride of copper, when all the uncombined iron is dissolved, and copper precipitated in its stead. When the solution has been poured off, the precipitated metal is digested, out of contact of air, with a neutral solution of sesquichloride of iron which redissolves the metallic copper.

When this residue is digested with potassa, the latter dissolves a newly formed brown humus-like substance, together with phosphoric acid, arsenic acid, and silicic acid. Almost the whole of the silicic acid may be determined in this residue.

It is yet to be ascertained whether this residue can be analyzed by heating in chlorine-gas.

109. ASH OF THE REFINING-HEARTH.

Crystallized = 3 FeO, SiO_2.

The analysis of pure crystals picked out of the mass is simple and easy, since they consist essentially only of protoxide of iron and silicic acid. They are finely powdered, and treated with hydrochloric acid and some concentrated nitric acid until they are completely gelatinized, the analysis being conducted as in the case of Lievrite. The sesquioxide of iron obtained is calculated as protoxide.

The quantitative analysis of the ordinary compact slag is far more difficult and complex, since it may contain, in addition to the above principal constituents, small variable quantities of the protoxides of copper, nickel, cobalt, and manganese, besides the oxides of chromium, molybdenum and vanadium, together with alumina, potassa, lime, magnesia, arsenic and phosphoric acids.

Several of these constituents can only be discovered by a qualitative analysis, for which a large amount of slag is employed. The process is conducted as follows:—

A pound of the slag, powdered as finely as possible, is intimately mixed with an equal weight of nitre, and as much carbonate of potassa,* and exposed for an hour, in a crucible, to a moderate red heat. The mass is finely powdered, boiled out with water, the solution filtered off, and the residue washed several times with hot water.

The solution may contain, besides alkaline carbonates and nitrites, vanadic acid, chromic acid, molybdic acid, arsenic acid, phosphoric acid, silicic acid, and alumina. A yellow color indicates the presence of chromic acid.

It is now carefully mixed with nitric acid, so that it may still remain alkaline, and any silica which may be precipitated is filtered off. A yellow color at this stage of the process denotes the presence of vanadic acid. The liquid is then evaporated to crystallization, and the greater part of the alkaline nitrate allowed to crystallize out in as cool a place as possible. The mother-liquor is poured off from the crystals, which are washed several times with a little perfectly cold water; the washings are mixed with the mother-liquor, and acetate of lead added as long as any precipitate is produced. This precipitate contains all the substances above enumerated, in combination with oxide of lead. It is filtered off and washed once or twice.

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* Perhaps smaller quantities of both might be employed.

Chromic and vanadic acids cannot be completely separated from oxide of lead by means of sulphuric acid. The precipitate is therefore treated, while still moist, with a mixture of fuming hydrochloric acid and strong alcohol, with which it is heated nearly to ebullition, when all the lead and silica are separated in an insoluble state, and the metallic acids are converted into green chlorides, and dissolved together with the phosphoric and arsenic acids. The chloride of lead is filtered off and washed with alcohol; the green solution is evaporated to the consistency of a syrup, mixed with a slight excess of a concentrated solution of potassa, and chlorine passed into it until the metallic oxides have redissolved in the form of acids, imparting a yellow color to the solution.* The liquid is then neutralized with ammonia, concentrated as far as possible by evaporation, allowed to cool, and a fragment of chloride of ammonium placed in it, so large as not to be entirely dissolved. The vanadic acid is thus almost completely precipitated as an ammonia-salt, in the form of a white or yellow crystalline powder. After twenty-hours it is filtered off and washed, first with a saturated solution of sal-ammoniac, afterwards with alcohol. It may be purified by dissolving in boiling water with the addition of some ammonia.†

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* Phosphate of alumina may precipitate here, and must be analyzed separately. (*See* No. 19.)

† It is possible that, if molybdenum be present, a yellow compound of phosphoric acid, molybdic acid and ammonia might be precipitated here. It is insoluble in hot dilute nitric acid. This circumstance might be made use of for separating the molybdic acid at once from the solution after treatment with chlorine. The solution would be mixed with ammonia, and afterwards boiled, with addition of nitric acid in slight excess, when the compound would separate as a yellow powder. It contains 3 per cent. of phosphoric acid.

When dry, it is very gradually heated in a shallow platinum dish to expel the ammonia, and the residual vanadic acid is fused at a low red heat. If pure, it solidifies, on cooling, to a dark brown-red, very crystalline mass.

The solution filtered from the vanadate of ammonia is mixed with ammonia, and afterwards with a solution of chloride of magnesium, which precipitates all the phosphoric, and most of the arsenic acid. After twenty-four hours, the precipitated double salts are filtered off, washed with dilute ammonia, dissolved in hydrochloric acid, the solution heated to 50°, and the arsenic precipitated by a stream of sulphuretted hydrogen-gas. In the filtrate from the sulphide of arsenic, the phosphoric acid may again be precipitated as a double salt by adding ammonia.

The solution filtered from the magnesia precipitate, which still contains the chromic and molybdic acids, is saturated with sulphuretted hydrogen and heated, when all the chromium is precipitated as green sesquioxide.

From the solution filtered from this precipitate, the molybdenum is precipitated by dilute sulphuric acid as a brown sulphide of molybdenum, from which, when heated in a tube, a mixture of sulphur and sulphide of arsenic sublimes, while black lustrous MoS_2 remains behind.

The residue of sesquioxide of iron which is left after ignition with nitre and alkali, and extraction with water, is partly dissolved by digestion with concentrated hydrochloric acid, and if sulphuretted hydrogen be passed through the solution, the copper will be precipitated.

The solution filtered from the precipitate is heated to the boiling-point, and a sufficient quantity of chlorate of potassa gradually added, to convert the protochloride of iron into sesquichloride. The small quantities of nickel, cobalt, and manganese which are present may be detected by precipitating the solution either with excess of ammonia or with carbonate of lime, when those metals remain in solution and may be precipitated by sulphide of ammonium.

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110. GLASS.

Silicates of CaO, and KO or NaO, frequently also, of PbO.

Two analyses are made, one by fusion with an alkaline carbonate, for the determination of silicic acid; the other by decomposing the glass with hydrofluoric acid, in order to estimate the alkali.

I. The very finely-powdered glass fused with three times its weight of carbonate of potassa and soda (No. 10), the mass softened in water, dissolved in dilute hydrochloric acid, evaporated to dryness, redissolved in water, acidulated with hydrochloric acid, the silica filtered off and washed.

From the solution, the small accidental impurities of sesquioxide of iron, oxide of manganese, and alumina, which are usually contained even in white glass, are precipitated by ammonia, after the solution has been mixed with some chlorine-water to peroxidize the protoxide of manganese.

The lime is afterwards precipitated by oxalic acid, and the solution filtered from the oxalate of lime is tested for magnesia, which may, moreover, have been precipitated with the alumina.

If the glass contain oxide of lead, that metal is precipitated by sulphuretted hydrogen from the solution filtered from the silicic acid.

II. For the determination of alkalies, a second quantity of the very finely-powdered glass is decomposed by hydrofluoric acid, or by ignition with carbonate of baryta, as in the analysis of feldspar, the subsequent process being also conducted as in that analysis, so that the other bases may, if necessary, be again determined here.

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111. CLAY.

$3\,Al_2O_3, 4\,SiO_2 + 6\,HO$, with variable quantities of KO, MgO, FeO, MnO, Feldspar, Sand, &c.

The water is determined by igniting the clay previously dried at 100°.

I. The clay is heated with concentrated sulphuric acid, the greater excess of acid evaporated, the residue dissolved in concentrated hydrochloric acid, by the aid of heat, and the silicic acid filtered off. If the clay contain an admixture of sand or feldspar, the silica is dissolved in a boiling concentrated solution of carbonate of soda, when the sand and feldspar remain undissolved.

The hydrochloric solution is considerably diluted, and gradually neutralized with carbonate of soda, as in No. 25, so that sesquioxide of iron and alumina are precipitated, while protoxide of manganese, lime, and magnesia, remain in solution as bicarbonates. The separation of alumina and sesquioxide of iron is then effected as in No. 21, that of the other bases as in No. 25.

II. The clay is fused with three times its weight of carbonate of potassa and soda (*see* No. 10), the fused mass dissolved in dilute hydrochloric acid, the solution evaporated to dryness, the residue dissolved in water containing hydrochloric acid, and the solution filtered off.

The separation of the other bases contained in the solution is then effected as in I.

III. For the determination of the alkali, a separate portion of the clay is decomposed by fusion with hydrate or carbonate of baryta, and the process conducted as in No. 80, the baryta and the other bases being precipitated from the solution by a mixture of ammonia and carbonate of ammonia; after gently heating, the precipitate is filtered off, the solution evaporated, and the residue ignited, when chloride of potassium and chloride of sodium are left. Or the analysis may be made with a mixture of hydrofluoric acid and hydrochloric acid.

112. COMMON LIMESTONE, HYDRAULIC LIMESTONE, MARL.

Carbonates of CaO, MgO, FeO, MnO, with Clay containing alkali, and sometimes $3\ CaO, PO_5$.

I. For the detection of the alkali, large fragments of the mineral, when it contains carbonate of lime in predominating quantity, are placed in a charcoal fire, and heated for half an hour to whiteness, when the clay, which contains the alkali, is decomposed.

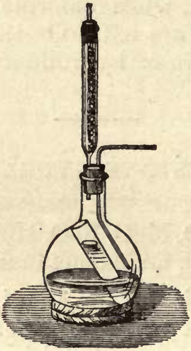
The ignited mass is carefully freed from adhering ash, powdered, exhausted with water, the solution mixed with some carbonate of ammonia, evaporated, the precipitated carbonate of lime filtered off, the solution acidified with hydrochloric acid, evaporated to dryness, and the residual chloride of potassium or sodium heated to dull redness. If both salts be present, they are separated by bichloride of platinum.

II. From a portion of the mineral which has been dried at 100° and weighed, the water is expelled by ignition in a glass tube, and its quantity determined by collecting it in a weighed chloride-of-calcium tube.

III. The carbonic acid may be expelled from another portion of the mineral by nitric acid in the apparatus employed for testing potashes, and its amount determined directly by the loss of weight. (Fig. 24.)

Or a weighed quantity of the substance is fused with about four parts, accurately weighed, of vitrified borax, in a platinum crucible, when all the carbonic acid is expelled, and its amount may be determined from the loss of weight, or if the water is expelled at the same time it must be taken into account in the calculation. (*See* No. 7.)

Fig. 24.



IV. Another very finely powdered portion is digested with very dilute nitric acid, which dissolves the carbonates, together with the phosphate of lime, leaving the clay, which is filtered off, ignited and weighed. It is then analyzed as in No. 111.

The separation of the other constituents present in the solution is effected as in No. 13.

113. IODIDE, BROMIDE, AND CHLORIDE OF SODIUM.

The solution is mixed with nitrate of protoxide of palladium, when all the iodine is precipitated as dark brown iodide of palladium, the bromide of palladium remaining in solution because chloride of sodium is present. After the lapse of twelve hours, the precipitate is collected upon a weighed filter, dried over oil of vitriol, or at a temperature not exceeding 80°, and weighed.

The excess of palladium in the filtrate is separated by means of sulphuretted hydrogen, in order to prevent the formation of a precipitate containing palladium upon the subsequent addition of nitrate of silver. The excess of sulphuretted hydrogen is then removed from the solution by sulphate of sesquioxide of iron, and the filtrate mixed with nitrate of silver, when a precipitate of chloride and bromide of silver is formed, which is collected, washed, dried, and fused. A quantity of this precipitate, weighed in a bulb-tube, is fused in a current of dry chlorine until bromine vapor ceases to be evolved, and the tube changes no longer in weight. Before weighing, every trace of chlorine must be removed from the bulb.

A simpler method consists in pouring water over the weighed mixture of bromide and chloride of silver, adding a few drops of hydrochloric acid, and a fragment of zinc. In twenty-four hours the silver is completely reduced; it is rubbed to powder, boiled with water containing hydrochloric acid, afterwards washed with pure water, ignited and weighed.

The difference between the equivalents of chlorine and bromine is to the equivalent of bromine, as the difference between the amounts of chloride and bromide of silver employed, and the amount of chloride which the reduced silver ought to yield, is to the amount of bromine present.

For example: 200 parts of a mixture of equal weights of chloride and bromide of silver gave, when reduced, 132.73 of silver, which would yield 176.31 of chloride of silver.

Difference between the equivalents of chlorine and bromine=44.5. Difference obtained=23.69. Then $44.5 : 80 = 23.69 : x$ (=42.5 bromine).

By the same indirect method, the amount of iodine contained in a mixture of iodide with chloride or bromide of sodium may be determined.

The iodine may also be determined in a mixture of chloride and iodide of potassium or sodium, by adding a solution of sulphate of copper mixed with sulphurous acid, when the iodine is precipitated as white subiodide of copper, which is then washed.

This method is also applicable for the approximative separation of iodine and bromine.

In order to detect iodic acid with nitric acid (*in nitrate* of soda), a little silver is dissolved in it. All the iodine remains as insoluble iodide of silver.

114. CRUDE COMMON SALT.

I. A weighed quantity of the moist salt is dried for some time at about 100°, then heated to about 300° in a covered crucible, and the water determined from the loss.

II. For the estimation of the sulphuric acid, the salt is dissolved in water (when any insoluble impurities are left), the solution slightly acidified with hydrochloric acid and precipitated by chloride of barium.

III. The lime is determined in a larger quantity of the salt, by precipitating it from its solution by oxalate of ammonia, and filtering off the oxalate of lime when it has subsided.

IV. The filtrate is concentrated by evaporation and mixed with ammonia and phosphate of soda to precipitate the magnesia; after the lapse of twenty-four hours, the precipitate is filtered off and washed with ammonia.

V. The very small quantity of potassa which is usually present, may be detected by concentrating the solution of a large quantity of the salt so that a great part of the chloride of sodium may crystallize out; the potassium is then precipitated from the mother-liquor with bichloride of platinum.

VI. The bromine may be detected by passing chlorine into the mother-liquor obtained from a large quantity of the saline solution, and agitating the liquid with ether, which takes up the bromine, and thence acquires a yellow color. The bromine may then be converted into bromide of ammonium by adding ammonia.

VII. In order to detect the iodine, the mother-liquor is mixed with some starch-paste, and weak chlorine-water added drop by drop; or the vapor of bromine or of nitrous acid may be allowed to flow on to the surface of the mixture.

For the quantitative determination of iodine and bromine, *see* No. 113.

115. INCRUSTATIONS FROM SALT-PANS.

$$NaCl, — NaO, SO_3, — CaO, SO_3, — MgO, SO_3, — CaO, CO_2, MgO, CO_2.$$

I. A weighed portion is heated nearly to redness in order to determine the water.

II. Another portion is finely powdered and boiled with water, the residual carbonates of lime and magnesia filtered off, washed with hot water, and the two bases separated as in No. 12. This residue sometimes contains iron and manganese.

III. The filtrate is mixed with chloride of ammonium, and the lime precipitated by oxalate of ammonia. (*See* No. 12.)

IV. The solution filtered from the precipitate is mixed with ammonia, and the magnesia precipitated by phosphate of soda. (*See* No. 6.)

V. Another portion of the incrustation is dissolved in hot dilute hydrochloric acid, and the sulphuric acid precipitated by chloride of barium (No. 3).

VI. A smaller quantity is dissolved in dilute nitric acid, and the chlorine precipitated by nitrate of silver (No. 1).

VII. The sodium and soda are calculated from the loss.

VIII. In order to detect a small quantity of sulphate of potassa, a large quantity of the incrustation is finely powdered, boiled with an excess of hydrate of baryta, the solution filtered off, the lime and baryta precipitated by a mixture of ammonia and carbonate of ammonia, the filtrate acidified with hydrochloric acid and evaporated to dryness; the residue is ignited, dissolved in water, and the solution treated with bichloride of platinum.

In this process also, the soda which previously existed as sulphate, may be obtained in the form of carbonate.

116. MINERAL WATERS, WELL-WATERS, SALINE SPRINGS.

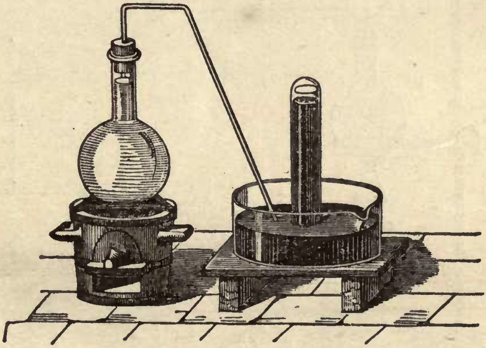
It is supposed that the analyst has an unlimited quantity of water at his disposal, so that separate portions may be employed for the determination of most of the individual constituents. For the estimation of those substances which are present in large quantity, small portions of water must be employed, larger quantities being taken for such constituents as exist in small proportion.

I. The *specific gravity* is first determined, in order to ascertain, by calculation, the weight of 10, 50, or

100 cub. cents. or grain measures of water, so that the quantities of water employed may be determined by measure.

II. *Carbonic acid and sulphuretted hydrogen-gases.*—The apparatus represented by Fig. 25 is used to determine the quantity of the air (nitrogen and oxygen) existing in the water.

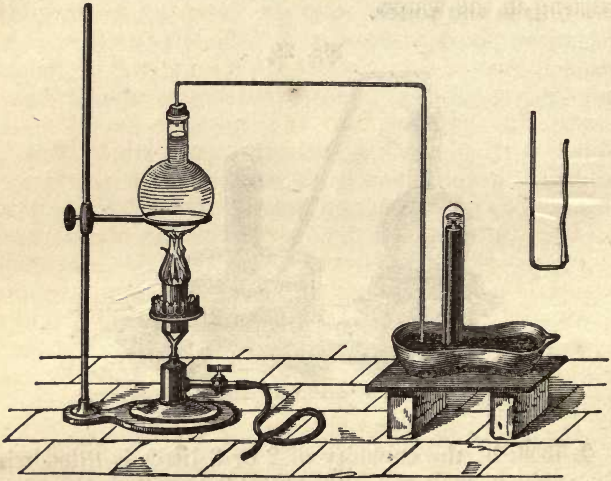
Fig. 25



A flask of the capacity of 2 or 3 litres is filled with the water as well as a tube suitable to collect the gases. When the apparatus is thus completely filled with water, the extremity of the bent tube is fastened under a graduated bell-glass full of mercury, and arranged over a mercury trough. The water is gently heated until it boils, and the air passes off with the stream and the quantity is seen in the graduated bell-jar.

The apparatus just described gives sufficiently exact results, when only the relation of the nitrogen and oxygen dissolved in the water is to be determined. It presents serious difficulties when carbonic acid is also to be determined; the water which is condensed in the tube being found in a sufficient quantity to dissolve this acid again in part or wholly. This difficulty may be avoided by making a very simple modification. A flask of the capacity from 400 to 500 cubic centimetres is used arranged as before.

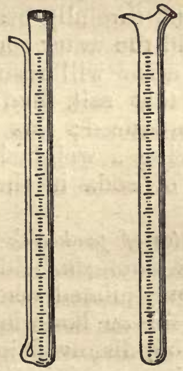
Fig. 26.



The apparatus being completely free from air, a caoutchouc tube is placed upon the end of the delivery tube to pass to the top of the small graduated bell-glass and kept there at a certain height.

The height is regulated on the supposed volume of gas that boiling furnishes. It is at first gradually heated so as to cause a small quantity of water to pass out from the flask, the volume of which is accurately measured and subtracted from the first volume taken; the delivery tube is then placed under the bell-jar, after which the temperature is gradually increased till the boiling point is reached. The bell-jar being nearly filled with gas and water which are evolved, the heat is instantly removed; a vacuum results from this which causes the return of condensed vapor into the flask. This absorption taking place, it is again heated. A certain quantity of gas is evolved which is added to that which the bell-glass already contains; when this is nearly full, the lamp is removed to determine the new absorption. This operation is repeated three or four times until the volume of the gas remains stationary. The caoutchouc tube is drawn down the bell-jar into the mercury so that the upper portion contains only the gases which were in solution in the water with a very small quantity of this liquid, which may be greatly diminished by introducing at the end of the operation some fragments of fused chloride of sodium. At length the gases contained in the bell-glass are measured, and the proportion of carbonic acid is determined by absorbing it by means of potassa.

Fig. 27.



Sulphuretted hydrogen.—The water may contain sulphur in two forms, either combined with hydrogen in the state of free hydrosulphuric acid, or combined with an alkaline metal (sulphide of sodium, potassium, &c.).

The sulphur of the hydrosulphuric acid, and that of the alkaline sulphides are in general determined at the same time by a method depending upon the decomposition of these compounds by free iodine and upon the coloration that the slightest possible trace of iodine in excess communicates to starch. A standard solution of iodine is made containing 1.27 grams of the iodine to a litre. 1 litre of this solution precipitates 0.16 gr. of sulphur, consequently, 1 cubic centimetre of it precipitates 0.00016 gr. A definite volume of sulphur water being placed in a flask a small quantity of starch is added to it; by means of a graduated cylinder, Fig. 27, the standard solution of iodine is gradually poured into the water, shaking the flask; a drop of iodine in excess colors the liquid permanently blue.

III. The *total weight of the fixed constituents* is ascertained by evaporating a measured quantity of the water to dryness, and carefully heating the residue to about 200°. Should the water contain much chloride of magnesium, an error will result from the partial decomposition of that salt, hydrochloric acid and magnesia being produced; this may, however, be avoided by dissolving a weighed quantity of pure ignited carbonate of soda in the water before evaporating.

IV. The *carbonates of protoxide of iron, protoxide of manganese, lime and magnesia,* held in solution by free carbonic acid, are precipitated when a large quantity of water is boiled for an hour in a flask. The precipitate is filtered off, dissolved in hydrochloric acid, the sesquioxide of iron precipitated by ammonia, and the protoxide of manganese, lime and magnesia separated as in No. 25.

V. The *silicic acid* is left undissolved on treating the residue obtained by evaporation, with dilute hydrochloric acid. Should the water contain carbonate of soda, it must be acidulated with hydrochloric acid previously to evaporation. If gypsum be present, a large quantity of water must be employed to redissolve it.

VI. *Boracic acid* may be detected by mixing the water with carbonate of soda, concentrating by evaporation to a small bulk, and acidifying with hydrochloric acid; if turmeric-paper be dipped in this solution, and dried, it will become brown if boracic acid be present.

VII. The presence of *nitric acid* may be detected by adding to the partially evaporated water or to the residual salts, a few drops of water, colored with a solution of sulphate of indigo, and mixed with some hydrochloric acid, which has been boiled. On boiling, the solution will be decolorized.

Some other bodies, especially free chlorine, have the same bleaching effect.

Or if the concentrated solution is mixed with several times its volume of pure strong sulphuric acid, the mixture allowed to cool, and then a few drops of a concentrated solution of sulphate of protoxide of iron cautiously added so that the fluids do not mix, a reddish purple or dark-brown stratum is produced according to the quantity of the acid present. Or the very concentrated solution may be heated with metallic copper and concentrated sulphuric acid, when yellowish red vapors of nitrous acid make their appearance. Or the dry residue may be mixed with anhydrous sulphate of copper or oxide of lead, and heated in a tube. If pieces of paper moistened with sulphate of protoxide of iron are held in the tube, they will be colored yellow or brown if nitric acid is present.

A very sensitive reaction consists in mixing the salt with some starch paste containing iodide of potassium and sulphuric acid. A small piece of bright zinc is placed in the mixture which reduces the nitric acid to nitrous, and gives the iodine reaction.

VIII. The *chlorine* is precipitated by nitrate of silver after acidifying the water with nitric acid; the precipitate is treated as in No. 1.

IX. *Bromine* and *iodine*, present only in very small quantity, can only be detected and estimated in large quantities of water, or in the mother-liquid. They are recognized as in Nos. 113 and 114. If the quantity of iodine present is very small a few drops of pure iodide of potassium and hydrochloric acid are added to the water, and the amyl reaction made. In order to concentrate the bromine, the water may be evaporated to dryness, and all the bromide of sodium, with but little chloride, extracted from the residue by absolute alcohol. When the alcohol has been evaporated or distilled off, the residue is dissolved in water, and a small quantity of nitrate of silver added, with constant stirring, so that only about $\frac{1}{6}$ of the chlorine may be precipitated as chloride of silver; the precipitate which contains all the bromine is weighed, and a certain portion of it analyzed as in No. 114.

X. The *sulphuric acid* is precipitated by chloride of barium from the water slightly acidified with hydrochloric acid.

XI. *Potassa* and *soda.*—The water is evaporated to about one-half, and mixed, without filtering, with excess of baryta-water; the mixture is allowed to cool, and carbonate of ammonia added; in this way, the sulphuric acid, lime, and excess of baryta are precipitated. The filtrate is acidified with hydrochloric acid, evaporated to dryness, and the residue, which is a mixture of chloride of sodium, chloride of potassium, and chloride of magnesium, is then cautiously heated to redness. The three metals are separated as in No. 11.

XII. *Carbonate of soda.*—The water is boiled for a long time, the precipitated earthy carbonates filtered off, and the filtrate divided into two equal parts. In one of these, previously acidified slightly with nitric acid, the chlorine is determined by precipitation with nitrate of silver. The other portion is mixed with a slight excess of hydrochloric acid, evaporated to dryness, and the residue heated nearly to redness; it is then dissolved in water and precipitated by nitrate of silver. The difference between this amount of chloride of silver and the former, corresponds to the quantity of carbonate of soda which was contained in the water.

XIII. *Lime.*—In the solution filtered from the precipitate obtained in IV., the lime is precipitated by oxalate of ammonia, after addition of ammonia. (*See* No. 12.)

XIV. *Magnesia.*—The solution filtered from the lime-precipitate is concentrated by evaporation, allowed to cool, mixed with concentrated ammonia, and the magnesia precipitated by phosphate of soda. (*See* No. 6.)

XV. *Lithia.*—The lithia is best obtained from the mother-liquid according to the method given in XI. The solution filtered from the precipitate is mixed with phosphate of soda, evaporated to dryness, and the residue treated with a very small quantity of water, when phosphate of soda and lithia is left, which should, however, be tested for magnesia.

Or the mother-liquor may be evaporated to dryness with excess of carbonate of soda, the residue extracted with hot water, the filtered solution mixed with phosphate of soda and evaporated to dryness.

XVI. *Strontia* may be sought in the ferruginous and calcareous stalactites and ochreous deposits from waters containing carbonic acid.

XVII. *Phosphoric acid.*—The foregoing remark applies also to the phosphates. Or a large quantity of water may be evaporated to a small bulk, mixed with ammonia, the precipitate filtered off, dissolved in nitric acid, and tested for phosphoric acid with molybdate of ammonia.

XVIII. *Arsenic acid,* in combination with lime or sesquioxide of iron, must likewise be sought, in the stalactites or ochres from such waters, with the aid of Marsh's apparatus. (*See* Poisoning by Arsenic.)

XIX. *Antimony* and *copper,* to be tested for in the deposit, by sulphuretted hydrogen.

XX. *Fluorine,* also contained in the deposit as fluoride of calcium. Or it may be sought in the precipitate obtained by ammonia in XVII., a part of which should be dried and moistened with concentrated sulphuric acid in a platinum crucible covered with a glass-plate coated with wax and marked in order to test for fluorine. (*See* No. 82.)

117. SOILS.

The ordinary constituents of soils, which differ much in different soils, and are very variable in quantity, are salts of chlorine, sulphuric acid, phosphoric acid, silicic acid, carbonic acid, nitric acid, with potassa, soda, ammonia, lime, magnesia, alumina, protoxide of manganese and protoxide of iron, together with sand and organic matters consisting of the *debris* of plants, and of the humous substances produced by their decay.

Some of these constituents are soluble in water.

Others are insoluble in water, but soluble in dilute acids, as, for example, the carbonates and phosphates of lime and magnesia.

The remainder are insoluble even in dilute acids;

these consist of quartz and of particles of feldspar, mica, and hornblende arising from the disintegration of different kinds of rock.

The soil to be examined is collected from different parts of the field, well powdered, allowed to dry in the air, and uniformly mixed.

It is most convenient to determine the greater number of the constituents in separate portions of the soil.

I. *Water.*—A weighed portion of air-dried soil is heated to 100°, and retained at that temperature till its weight is constant. In this way the amount of hygroscopic water is ascertained.

In order to determine the combined water in the salts, clay, &c., the soil may be heated to 200° or 300°, when the ammonia also may be expelled.

II. *Organic matters.*—The dry soil is ignited with access of air, moistened with carbonate of ammonia, and again heated nearly to redness. The loss in weight (ammonia and nitric acid being taken into account) indicates the total amount of organic matter.

The amount of nitrogenized organic matter can only be determined by ultimate analysis, when the ammonia and nitric acid must not be neglected in the calculation.

Certain organic substances, such as fatty and resinous matters, may be extracted from the dried soil by hot alcohol and ether.

The humous substances may be extracted by boiling the soil with solution of potassa; they are separated, though not completely, from the brown filtered solution, in the form of a brown precipitate, on adding hydrochloric acid.

III. *Ammonia.*—The soil is distilled with solution of soda, and the ammonia collected and determined as in No. 5.

IV. *Nitric acid.*—The analyst must be satisfied with the qualitative detection of nitric acid. The soil is extracted with water, the filtered solution evaporated to a small bulk, and the reactions made, given under nitric acid, No. 116.

V. The *constituents soluble in water.*—A large quantity of the air-dried soil, from 1000 to 2000 grammes, is heated nearly to ebullition, with water, for a considerable time; the residue is filtered off and thoroughly washed with hot water. The whole liquid is evaporated to about its original volume, carefully weighed or measured, and separate portions of it, weighed or measured off, are employed for the determination of the following constituents.

a. The *total weight* of the portion soluble in water is ascertained by evaporation to dryness.

b. Sulphuric acid is precipitated by chloride of barium from the solution acidified with hydrochloric acid.

c. Chlorine is precipitated by nitrate of silver, after acidification with nitric acid.

d. Silicic acid.—The solution is mixed with hydrochloric acid, evaporated to dryness, the residue extracted with dilute hydrochloric acid, and the silica filtered off.

e. Lime, magnesia, alumina, protoxide of iron, and *protoxide of manganese* may be contained in the filtrate from *d;* they may be separated as in No. 81.

f. Potassa and *soda.*—The solution is mixed with hydrochloric acid, evaporated to dryness, the residue dissolved in a little water, baryta-water added in excess, the mixture digested for some time, filtered off, and the baryta and lime precipitated from the filtrate by carbonate of ammonia. The solution filtered from these can contain only potassa and soda, which are estimated as chlorides, and are separated as usual.

g. Phosphoric acid, which can only be present if the solution contain no lime, &c., is precipitated as phosphate of magnesia-ammonia.

VI. *Constituents insoluble in water, but soluble in dilute hydrochloric acid.*—From 50 to 100 grms. of the residue obtained in V. (previously washed, dried, and uniformly mixed), are weighed off, mixed with water, in a flask, to a thin paste, heated, and hydrochloric acid gradually added until the effervescence ceases; the mixture is then heated for some time, with frequent agitation, the insoluble residue filtered off and well washed. The solution is concentrated by evaporation, weighed or measured, and divided into separate portions for the different determinations. If the soil contain much organic matter, it must be feebly ignited with access of air previously to the extraction with hydrochloric acid.

a. Silicic acid.—The solution is evaporated to dryness with addition of some nitric acid.

b. Sulphuric acid.—From a weighed portion of the acid solution, filtered from the silica, the sulphuric acid is precipitated by chloride of barium.

c. Alkalies.—Another portion of this solution is treated as in V., *f*, with baryta-water.

d. Phosphoric acid, lime, magnesia, alumina, protoxide of manganese, and *protoxide of iron,* are separated and determined in the greater portion of the solution filtered from the silica, according to the method given in No. 26.

e. The *carbonic acid,* may be determined in a separate portion of the washed soil, as in alkalimetrical examinations.

f. A small quantity of copper and arsenic sometimes contained in the soil may be determined by a special experiment. (*See* No. 26.)

VII. *Constituents insoluble in dilute hydrochloric acid.*—A small quantity (about 5 or 10 grms.) of the residue obtained in VI., is heated with several times its weight of concentrated sulphuric acid, until the greater part of the acid has been expelled. By this treatment the clay is decomposed. The nearly dry residue is digested with dilute hydrochloric acid, the solution filtered off, and analyzed as above, omitting the determination of silicic acid.

The residue left by hydrochloric acid is boiled for a long time with a concentrated solution of carbonate of soda, which dissolves the silica separated by the sulphuric acid. The filtered solution is acidified with hydrochloric acid, evaporated to dryness, and the silica filtered off.

The portion insoluble in carbonate of soda may be a mixture of sand, feldspar, and other minerals not decomposed by sulphuric acid, which may be separated to some extent with the aid of a magnifier. In order to decompose them they must be treated as in the analysis of feldspar, No. 80.

The greater part of the residue obtained in VI., previously to treatment with sulphuric acid, may be mechanically separated, with tolerable accuracy, into its constituents, by levigation. The residue is stirred up with much water by means of a feather, and the finer suspended portions, consisting chiefly of clay, are repeatedly poured off until only the grains of sand, feldspar, &c., remain behind.

118. ASHES OF PLANTS.*

Salts of KO, NaO, CaO, MgO, Al_2O_3, Fe_2O_3 and MnO, with Cl, F, SO_3, CO_2, and SiO_2.

Manganese does not occur in all ashes, and is seldom present in sufficient quantity to determine. Fluorine has been hitherto found only in the stalks of some of the *Graminaceæ*. Alumina is an essential constituent of the ashes of the *Lycopodiaceæ*, but is seldom present in appreciable quantity in other ashes. Even iodine, bromine, oxide of copper, and titanic acid have been found, though generally in very minute quantities, in some ashes.

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* By Professor Städeler.

The process of analysis differs according as the ashes do or do not contain more phosphoric acid than is requisite to combine with the sesquioxide of iron, protoxide of manganese, lime, magnesia, and alumina. To the former (containing more phosphoric acid) belong those of seeds, to the latter, those of woods, succulent plants, &c.

I. *Ashes of seeds.*—About 50 grms. of the seeds which have been dried in the air, or at 100°, are thoroughly carbonized by gentle ignition in a platinum crucible; the carbonaceous mass is powdered, moistened with water, and exposed for some time to the air, when the sulphides are converted into sulphates; it is then digested with concentrated acetic acid, water added, the mixture filtered, and the residue washed with hot water till the washings are only slightly acid to test papers. The carbonized mass is thus entirely, or almost entirely, freed from metallic chlorides; it is introduced, while yet moist, into a platinum crucible, and incinerated as far as possible by a protracted gentle ignition. (At a bright red heat, phosphide of platinum is formed and the crucible corroded.) Finally, a few drops of concentrated nitric acid are added to the ash, which is then ignited in the crucible, the cover of which is placed against its mouth, until the last traces of carbon are burnt off, and a perfectly white ash remains. This ash is added to the saline mass obtained by evaporating the acetic solution; the mixture is gently ignited to decompose the acetates, and weighed.

The ash is dissolved by nitric acid in a carbonic acid apparatus, and the carbonic acid determined from the loss.

The solution is mixed with 10 or 12 volumes of water, and the residue, consisting of undissolved silica (sometimes also of sand) and charcoal, is collected upon a filter (previously dried at 100°), weighed, carefully removed from the filter, and digested with very dilute solution of soda, which readily dissolves all the silica, except that present in the form of sand; the residue of sand and charcoal is collected upon the filter previously employed; its weight, after being dried at 100°, is deducted from the total weight of the ash. The weight of the silicic acid is determined from the loss.

From the filtered solution containing the saline constituent, the chlorine is precipitated by nitrate of silver, an excess of the precipitate removed by hydrochloric acid, the sulphuric acid precipitated by chloride of barium, and the excess of baryta separated by careful addition of sulphuric acid.

The filtrate is evaporated to dryness, the residue treated with concentrated hydrochloric acid, and digested with it for some time, in order completely to expel the nitric acid, and to convert any pyrophosphoric acid into the tribasic form. The hydrochloric acid is expelled as far as possible, a sufficient quantity of water afterwards added, and the solution filtered from the undissolved silica, which is ignited, weighed, and calculated together with that previously obtained.

From the solution, the iron, manganese, alumina, lime, and magnesia, are precipitated by ammonia as phosphates, which are collected, after six or eight hours, upon a filter, ignited and weighed. The precipitate is dissolved by digestion with concentrated hydrochloric acid, the free acid nearly neutralized with soda, and the solution mixed with acetate of soda, when the phosphates of sesquioxide of iron and alumina are precipitated. These are ignited and weighed, and if necessary (unless the ignited precipitate has a pure brown color), separated according to No. 19.—From the filtrate, the lime is precipitated by oxalate of ammonia, and the magnesia as phosphate of magnesia-ammonia, by merely adding an excess of ammonia; the phosphoric acid previously in combination with the lime is calculated from the loss.—If manganese be present, it is precipitated together with the phosphate of magnesia-ammonia, to which it imparts a gray or black color after ignition. The separation is effected as in No. 26.

The solutions from which the phosphates have been precipitated by ammonia, now contain only the alkalies and the remainder of the phosphoric acid. The latter is precipitated (together with sulphuric acid) by chloride of barium, and the excess of baryta removed by sulphuric acid or by neutral carbonate of ammonia; the filtrate is evaporated to dryness, the residue ignited, and the alkalies weighed as chlorides or sulphates. For their separation, *see* No. 4.—The precipitate produced by chloride of barium is exhausted with nitric acid, sulphuric acid added to effect the complete separation of the baryta, and the phosphoric acid precipitated from the filtrate, previously mixed with an excess of ammonia, as phosphate of magnesia-ammonia.

II. *Ashes of wood, vegetables, &c.*—Of those vegetables which yield a large amount of ash, 50 grms. may be taken for examination; but of the different kinds of wood, which are usually poorer in mineral constituents, and of the *Graminaceæ*, the ash of which contains much silica, about 100 grms. should be employed. The substances are carbonized in a platinum crucible, and the mass thrown immediately into a flat porcelain dish, where it generally smoulders for a long time, and is, for the most part, converted into ash. The incineration is completed in the platinum crucible.

The analysis of these ashes only differs from that of the preceding in that these contain a larger quantity of the alkaline earths than is necessary to combine with the phosphoric acid, so that the total amount of that acid is separated upon adding ammonia. The precipitate is *immediately* filtered off, and the filtrate mixed, first with sulphide of ammonium, to precipitate the manganese, then with oxalic acid for the lime, and lastly with phosphate of ammonia to separate the magnesia. Any excess of phosphoric acid may be separated, as directed above, from the alkalies, which are then weighed as chlorides or sulphates.

The stalks of the *Graminaceæ* usually leave an ash which cannot be completely decomposed by nitric or hydrochloric acid. The weighed silicate remaining undissolved, is decomposed most conveniently with hydrofluoric acid, and the bases, previously in combination with silicic acid, may then be estimated in the solution. The silicic acid is determined from the loss. In this case, the determination of the charcoal and sand must, of course, be omitted.

(See also for other, and, in part, newer and better methods, Liebig's and Kopp's Jahresbericht, 1850, p. 603; 1857, p. 582 and 584; 1859, p. 693.)

119. GUANO.

Guano consists of the partially decomposed excrement of sea-birds. It contains a great many substances, some soluble, others insoluble in water. The constituents upon which depend its important action and application as a manure are: organic, chiefly nitrogenized matters; salts of ammonia; phosphates, especially phosphate of lime; and salts of the alkalies. The amount of these constituents indicates the value of the guano. It is important to test this manure, since different specimens consist not only of various kinds of genuine guano of different degrees of richness, but samples also come into the market which are adulterated with common earth, loam, lime, sand, pebbles, and crude common salt or Glauber's salt.

Genuine guano presents the appearance of a moist yellowish-brown earth, mixed here and there with white fragments or lumps. Very few and rare specimens are white. It has a peculiar excrementitious or urinous odor, and a feeble penetrating saline taste.

It is chemically tested in the following manner:—

I. The guano is mixed, in a dish, with hydrate of lime (slaked lime stirred with water to a thin cream), when it should emit, especially when heated, a powerful odor of ammonia. In order to compare different specimens, the same quantity, say ¼ oz. of each, is taken. Since the value depends partly upon the amount of ammonia present, the better sorts of guano will evolve the stronger odor of that gas.

II. Two ounces (or from 50 to 60 grms.) of guano, finely powdered and uniformly mixed, are weighed in a counterpoised porcelain capsule, and heated on a water-bath until it is perfectly dry and suffers no farther diminution of weight. The loss of weight expresses the amount of moisture contained in the guano. Good guano loses only between 8 and 15 per cent. of water, but if fraudulently moistened, it may lose 20 per cent., or even more.

III. Half an ounce (or from 15 to 20 grms.) of guano is weighed, and heated over a large spirit-lamp, or gas-burner, in a porcelain or platinum crucible, with free access of air, until all organic matter has burnt off, and the guano is converted into a white or grayish ash. Good guano, when treated in this way, leaves from 30 to 35 per cent. of ash, while bad guano leaves from 60 to 80 per cent., and that which has been fraudulently adulterated leaves still more. The ash of genuine guano, whether of good or bad quality, is always white or grayish; a yellow or reddish color bespeaks an admixture of clay or earth. Good guano, when first heated, evolves white vapors, with a powerful odor of ammonia.

IV. A similar quantity of guano is mixed, in a dish, with several times its volume of water; heat is then applied, and the mass thrown upon a small filter (previously dried in the water-bath and weighed); the residue on the filter is washed with hot water till a small portion of the washing-water is not rendered turbid by adding chloride of calcium and ammonia. The filter, with the washed guano, is then thoroughly dried in a water-bath and weighed. The better the quality of the specimen, the less insoluble residue will be obtained. Good samples of guano leave from 40 to 45 per cent., those of bad quality as much as 70 or 80. If the guano be adulterated with common salt or with Glauber's salt, it will behave to this test like a genuine specimen, but furnish a greater quantity of ash in Experiment III.

V. The guano under examination, may be treated with moderately strong hydrochloric acid. Good guano effervesces but slightly; a specimen of guano adulterated with chalk, would effervesce strongly, and would leave a proportionally larger quantity of ash in Experiment III.

VI. The ash obtained in III. is dissolved in dilute hydrochloric acid, which should give rise only to slight effervescence, if the guano be unadulterated. The solution is filtered from the residue, the latter washed, dried, thoroughly burnt, together with the filter in a weighed crucible, over the spirit-lamp, and weighed. This insoluble residue, consisting partly of sand, amounts, in good (undried) guano, to only 1 or 2 per cent.

VII. The filtered hydrochloric solution is mixed with a slight excess of ammonia. The precipitate thus produced consists almost entirely of phosphate of lime. It is filtered off, washed, dried, and ignited; its quantity in good guano amounts to 20 or 25 per cent.

VIII. The filtrate from this precipitate should furnish only slight indications of lime on addition of oxalic acid; but if the guano be adulterated with chalk, this reagent will produce a very considerable precipitate. This solution ought therefore to contain only the alkaline salts, amounting to 5 or 10 per cent. of the original undried guano. In order to determine them directly, which is generally unnecessary for practical purposes, the solution must be mixed with some more chloride of ammonium, and evaporated to dryness; the residue is heated to volatilize the excess of chloride of ammonium, and to convert the sulphates into chlorides, weighed, and farther treated as in No. 4.

IX. The aqueous solution, which was obtained in the lixiviation-test (IV.), and of which a fresh quantity may be prepared so as to be saturated, has a brown color and a saline taste. When evaporated it evolves ammonia, emits a urinous odor, and leaves a brown crystalline mass, consisting chiefly of sulphates of potassa and soda, chloride of ammonium, oxalate and phosphate of ammonia. This solution exhibits the following reactions:—

When mixed with hydrate of potassa, it smells strongly of ammonia.

With chloride of ammonium, ammonia, and sulphate of magnesia, it gives an abundant pulverulent precipitate or phosphate of magnesia-ammonia.

When acidified with acetic acid and tested with chloride of calcium, it gives a copious precipitate of oxalate of lime.

After addition of excess of hydrochloric acid, it gives, with chloride of barium, a considerable precipitate of sulphate of baryta.

X. When guano is exahusted with cold water, and the residue digested with a weak solution of caustic soda, uric acid is extracted. The solution is filtered, and feebly acidulated with hydrochloric acid, when the uric acid is precipitated. After being filtered off and washed, it is easily soluble in caustic potassa, and may be reprecipitated by hydrochloric acid. If it be dissolved in warm dilute nitric acid, the solution evaporated to dryness, and the residue moistened with carbonate of ammonia, a fine purple-red color is produced.

XI. The quantity of organic matter can be estimated directly only by an ultimate organic analysis. In good undried guano it amounts, taking the ammonia into account, to about 50 per cent.

XII. The exact determination of the nitrogen requires also an ultimate analysis. This element should amount to 12 or 14 per cent.; bad samples contain only from 1 to 6 per cent. The quantity of nitrogen, may, however, be approximately determined by the following method, which therefore allows us to ascertain rapidly the value of different specimens of guano. It depends upon the circumstance that when guano is treated with a solution of chloride of lime (hypochlorite of lime), the nitrogen of the organic matter and of the ammoniacal salts is evolved as gas.* Instead of collecting and measuring the gas evolved, which would be scarcely practicable, on account of the violent effervescence, the volume of water which is expelled by the gas is ascertained by means of the simple apparatus represented in the figure; it consists of a flask capable of containing about ½ pint, provided with a narrow

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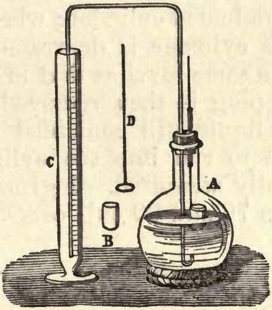
* Farther experiments are required to show that all the nitrogen is here evolved in the gaseous state, and to ascertain how the various nitrogen-compounds behave with chloride of lime.

Fig. 28.



gas-delivery-tube bent twice at right angles. One limb, rather the shorter of the two, is passed, air-tight, through the cork of the flask, and bent upwards to prevent, as far as possible, the escape of bubbles of gas. This tube descends nearly to the bottom of the flask. A second very narrow short tube is also passed through the cork, and serves for the escape of air when the cork is introduced. The longer limb of the delivery-tube dips into a tall cylinder or tube, which is graduated to cubic centimeters, or cubic inches. The flask is half-filled with solution of chloride of lime;* 1 grm. of guano is then weighed in the small glass vessel (the end of a test-tube) in which a few small shot have been placed, in order that it may float upright. With the aid of the handle of iron-wire shown in the figure, the tube is let down so as to float upon the surface of the solution of chloride of lime; the cork with the tube is then tightly adjusted, the orifice of the smaller tube closed with wax, and the flask shaken so that the little vessel may fill and sink. A volume of liquid equal to that of the nitrogen evolved from the guano then flows into the graduated cylinder; when no more liquid passes over, the cylinder is depressed so as to bring the liquid to the same level as that in the generating-flask; the wax plug is then removed, the cork withdrawn, and the liquid still contained in the delivery-tube is allowed to run into the cylinder, where the whole is carefully measured. 1 grm. of good guano evolves between 70 and 80 cub. cents. of gas.

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* This solution must be carefully prepared and kept in a dark place, in a closed vessel. It must contain an excess of hydrate of lime, and therefore need not be perfectly clear.

120. OXALATE AND PHOSPHATE OF LIME.

A mixture of these two salts dissolves in nitric acid without effervescence, and is precipitated from the solution by ammonia. If it be digested, when freshly precipitated, with acetic acid, the phosphate of lime may be dissolved, while the oxalate is left.

If the mixture be previouly ignited, it dissolves in nitric acid with effervescence, and ammonia then precipitates from the solution only the phosphate of lime, while the lime which had been in combination with oxalic acid remains in solution, and may be precipitated by oxalate of ammonia, and quantitatively determined. Phosphate of lime, when freshly precipitated, may be recognized by the yellow color which it assumes when moistened on the filter, with nitrate of silver. It is analyzed as in No. 13.

If the two salts be dissolved in the smallest possible quantity of hydrochloric acid, and the solution mixed with an excess of acetate of soda, the oxalate of lime is precipitated, while the phosphate remains in solution; from the latter, the lime may be precipitated by oxalate of ammonia, and afterwards the phosphoric acid by sulphate of magnesia and ammonia, as in No. 9.

When the mixture of the two salts is treated with concentrated sulphuric acid, oxalic acid is converted into carbonic acid and carbonic oxide, so that by employing the apparatus described in the article upon alkalimetry, its amount may be inferred from the loss of weight.

By gently heating the mixture with an excess of finely-powdered binoxide of manganese or neutral chromate of potassa, or with binoxide of lead and dilute sulphuric acid, all the oxalic acid is converted into carbonic acid, the quantity of which may be determined by the use of the apparatus above alluded to. 2 equivs. of carbonic acid correspond to 1 equiv. of oxalic acid.

If binoxide of lead be employed in this operation, the quantitative determination of the phosphoric acid may be effected at the same time; for this purpose, the mixture is digested for some time, to liberate the whole of the phosphoric acid; several volumes of alcohol are then added, in order to separate the sulphate of lime, the solution filtered, and the residue washed with alcohol. From the filtrate, after the evaporation of the alcohol, the phosphoric acid may be precipitated by sulphate of magnesia and ammonia.

A very accurate method of estimating oxalic acid consists in converting it into carbonic acid by means of a solution of terchloride of gold, weighing the reduced gold, and calculating thence the amount of oxalic acid; 3 equivs. of the latter reduce 1 equiv. of gold = 197.

For this purpose the mixture of the two salts is dissolved in the smallest possible quantity of hydrochloric acid (a large excess impedes the reduction in gold), mixed with an excess of a solution of terchloride of gold, or better, of sodio-chloride of gold, diluted with much water, and heated to ebullition. The reduced coherent gold is easily washed; it is to be dried, ignited, and weighed.

The excess of gold is removed from the solution by sulphuretted hydrogen, or by boiling with oxalic acid, and the phosphoric acid and lime are then separated and estimated as in No. 13.

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121. ALKALIMETRY.

The specimens of potashes and soda-ashes met with in commerce contain very variable quantities of foreign substances. The amount of carbonated alkali, upon which their value alone depends, varies between 40 and 95 per cent.

The potashes contain chiefly chloride of potassium, sulphate, silicate, and phosphate of potassa, and carbonate, phosphate, and silicate of lime.

The soda generally contains chloride and sulphide of sodium, sulphate, silicate and hyposulphite of soda, and often also hydrate of soda.

The amount of alkaline carbonate present in the sample, may be determined by several methods.

I. *By the standard solution test,* i. e., *by exactly neutralizing a weighed portion with dilute sulphuric acid of known strength.*

In order to prepare the test-acid, a known quantity, say 70 grms. of concentrated sulphuric acid, are diluted with 600 grms of water.

5 grms. of pure anhydrous carbonate of soda are weighed, dissolved in *hot* water, and the solution colored blue with a little tincture of litmus.

The test-acid is then added to the solution, from a burette, very carefully as the point of neutralization is approached, until the color is just changed to red, and streaks which are made with the liquid upon litmus-paper, remain red after drying.

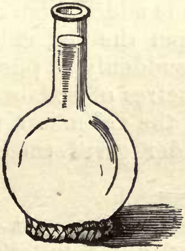
The number of measures of acid employed is then observed, and the whole of the test-acid is diluted with so much water, that exactly 100 measures are required to neutralize 5 grms. of pure carbonate of soda. This stock of test-acid is preserved in a well-stopped bottle. It indicates immediately the percentage of caustic or carbonated alkali in a specimen of potashes or soda, provided that a quantity of the sample be employed, which is equivalent to 5 grms. of carbonate of soda.

100	**measures**	**of test-acid**	**saturate**	**5.000**	**grms.**	**of carb. of soda.**
100	**"**	**"**	**"**	**2.935**	**"**	**of soda.**
100	**"**	**"**	**"**	**6.487**	**"**	**of carb. of potassa.**
100	**"**	**"**	**"**	**4.421**	**"**	**of potassa.**

So that if 6·487 grms. of a sample of potashes be taken, the number of measures of acid employed will express, directly, the percentage of carbonate of potassa, or if 4.421 grms. be used, of anhydrous potassa, contained in the specimen.

Instead of sulphuric acid, pure crystallized oxalic acid may be very conveniently employed for preparing the test-solution. An equivalent of the acid (63 grms.) is introduced into a flask of 1 litre capacity, which is then two-thirds filled with water; the acid is allowed

Fig. 29.



to dissolve, and so much water added that the whole solution may measure 1 litre or 1000 cubic centimetres, at 17.5° C.

One hundred cub. cents. of this test-acid will then exactly neutralize $\frac{1}{10}$ of an equivalent proportion of either alkali. It is therefore necessary to weigh out $\frac{1}{10}$ of an equivalent proportion (in grammes) of the anhydrous alkali to be tested, that is, 6·92 grms. of potashes, or 5·32 grms. of soda-ash. In order to obtain perfectly accurate results, the process is conducted as follows: The solution of alkali to be tested, is introduced into a flask colored, with tincture of litmus, and the test-acid poured into it from a burette, until the color changes from blue to violet, and the effervescence is very feeble. The solution is now heated to ebullition, and more acid added until the color has become decidedly red. 5 or 10 cub. cents. of the test-acid are then added in excess; the alkali will be now supersaturated. By boiling, agitating, and finally sucking out with a glass tube, the last traces of carbonic acid are removed [illegible] now required to determine exactly how far the neutralization of the alkali has been exceeded; for this purpose a standard solution of caustic soda is employed, of such strength that it is exactly neutralized by an equal volume of the test-acid;* this solution is added from a burette graduated to $\frac{1}{10}$ cub. cent., when the red color rapidly changes to violet, and then suddenly to pure blue. The number of cubic centimetres of soda-solution employed, is then deducted from the volume of test-acid previously added; the remainder gives the percentage of pure alkaline carbonate.

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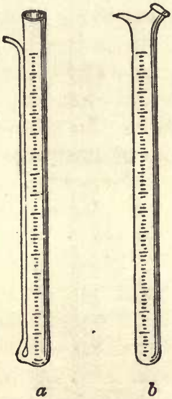
* This solution of soda must be perfectly free from carbonic acid. In order to preserve it in that state, the bottle is closed with a cork, through which passes an ordinary chloride-of-calcium-tube, open at both ends, and filled with a mixture of Glauber's salt and quicklime in powder.

The dropping-tubes or burettes employed for these analyses with standard solutions, are made of different forms. The commonest is that represented in Fig. 30 *a*, and consists of a glass tube, closed at one end, about 0.25 metre (or 12 inches) long, and 0.01 metre (or $\frac{1}{2}$ inch) in diameter; into the lower part of this tube is cemented another, very much narrower, which is fixed parallel with the larger tube; the extremity of the small tube is bent outwards and sharply cut off, so that the liquid may be conveniently poured from it. The whole of the vessel is divided into known volumes, and it is preferable to take from 25 to 50 cub. cents., and to divide these into fractional parts. The zero should be placed at the top of the scale, below the level of the orifice of the spout.

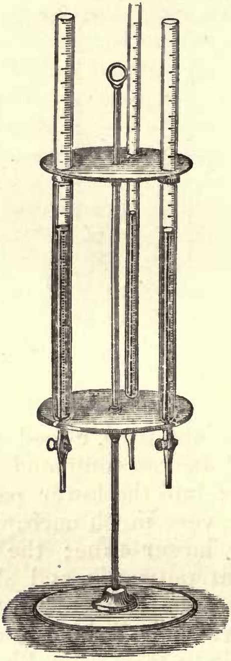
Fig. 30.



Another form is that shown in Fig. 30 *b*, which consists of a single divided tube furnished at the top with a spout, and with an orifice for pouring in the liquid.

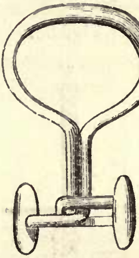
A third form of burette, which is the most suitable and convenient, and can be very easily made by the analyst himself, is that represented by the adjoining figure. It consists of a glass tube, about 0.01 metre in diameter, which is divided into 25 or 50 cubic centimetres, and drawn out to a point at the lower extremity. To this open point is attached a narrow tube of vulcanized caoutchouc, about an inch long, and in the lower end of this tube is inserted a short glass tube drawn out to a narrow point and cut smoothly off; this tube serves for dropping the liquid out, and is

Fig. 31.



tightly connected with the graduated tube in such a manner that a considerable interval may be left between the ends of the two tubes. Upon this part of the caoutchouc tube is fixed a clamp made of thick brass wire, shown with its actual dimensions, in the accompanying figure, so constructed that the caoutchouc tube may be opened by pressing upon the two ends of the clamp, and closed when the pressure is removed. In order to use this tube, it is fixed in a stand, in a vertical position, above the vessel containing the liquid to be tested. By pressing upon the ends of the little clamp, the caoutchouc tube is opened, and the liquid allowed to flow out, even in single drops, if required. At the commencement of the operation, the tube is filled with the test-liquid, a portion of which is then made to flow out, by pressing upon the clamp until it stands exactly at the zero of the scale.

Fig. 32.

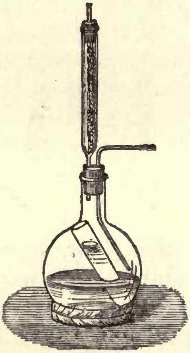


II. *By determining the carbonic acid evolved.*

The carbonic acid is liberated from a weighed portion of the alkali, in an apparatus which is previously weighed (together with the acid used to effect the decomposition), and the carbonic acid determined from the loss of weight.

The apparatus employed for this purpose may be arranged in different ways. That represented in the adjoining figure, of about ⅓ its real dimensions, will render apparent the general principle, upon which they are constructed, and will itself fully answer the purpose. It consists of a small light flask, closed by a cork perforated with two holes, in one of which is inserted a tube filled with fragments of chloride of calcium, and in the other, a narrow glass tube, running nearly parallel with the inner wall of the flask, and reaching almost to the surface of the liquid; above the cork, this tube is bent at right angles.

Fig. 33.



The specimen to be examined is weighed in the flask, the latter about one-third filled with water, and the small tube full of acid introduced with a pair of pincers; this tube must be of such a length that it cannot fall down in the flask, but may assume the position indicated in the figure. Sulphuric acid is to be preferred for effecting the decomposition of the carbonate, and should be employed in quantity more than sufficient to expel the whole of the carbonic acid. (For the carbonates of lime, baryta, and lead, nitric acid must be employed).—The cork, with the chloride-of-calcium-tube, and the bent tube is then introduced, air-tight, into the neck of the flask, the whole apparatus accurately weighed, and the orifice of the bent tube perfectly closed with a small cork or with wax.

The flask is then carefully inclined so that a small quantity of the acid may run out of the tube and decompose the carbonate. The carbonic acid which is evolved escapes through the chloride-of-calcium-tube, in which any water which may have been carried off with it is retained. No fresh acid is allowed to flow out of the tube until the effervescence caused by the first portion has ceased, and does not recommence upon gentle agitation. When, at length, the effervescence has entirely ceased, so that the salt is completely decomposed, the plug is removed from the small tube and suction applied, by the mouth, to the tube containing chloride of calcium, until the air passing through the flask no longer tastes of carbonic acid. In very exact experiments, a second chloride-of-calcium-tube must be attached to the small bent tube, to retain the moisture of the air.

1. *Potashes.*—The amount of water is ascertained by heating the specimen, for some time, to about 200°. For this purpose from 2 to 5 grms. of potashes may be taken.

In order to determine immediately, without calculation, the percentage of potassa in carbonate of potassa, by means of the above apparatus, 3.14 grms. of the specimen must be taken. Since 3.14 grms. of *pure* carbonate of potassa evolve 1.00 grm. of carbonic acid, the number of centigrammes of carbonic acid evolved will represent the percentage of carbonate of potassa.

2. *Soda.*—2.41 grms. of soda are employed. This is the quantity of *pure* carbonate of soda which evolves 1.00 grm. of carbonic acid.

Should caustic soda be contained in the specimen, which may be known by the alkaline reaction of the solution after adding an excess of chloride of barium, the following modification of the process is necessary:

2.41 grms. of the anhydrous sample are mixed with about 3 parts of pure quartz-sand, and about ⅓ part of powdered carbonate of ammonia; the mixture is moistened with water, and, after some time, gently heated till all water and ammonia are expelled. The dry residue is then treated, as usual, in the above apparatus.

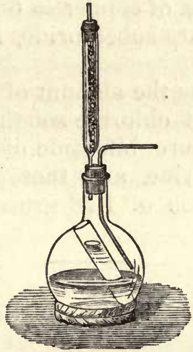
In order to prevent any inaccuracy arising from the presence of sulphide of sodium or hyposulphite of soda in the specimen, a solution of chromate of potassa is added previously to the evolution of carbonic acid, in order to oxidize these impurities.

122. VALUATION OF MANGANESE ORES.

Good manganese ore, which consists almost entirely of binoxide of manganese, is crystalline, yields a black powder, and, after being dried at a gentle heat, gives no water, or only traces, when heated to redness. Manganese ore, however, generally contains foreign minerals, especially the hydrated sesquioxide of manganese. In order to determine the amount of binoxide, or, in other words, of available oxygen, several methods may be employed.

I. A weighed quantity of the manganese ore, powdered as finely as possible, is introduced into the apparatus employed for the quantitative estimation of carbonic acid (Fig. 34), where it is brought in contact with sulphuric acid and a solution of oxalic acid, when sulphate of protoxide of manganese is produced, since all the available oxygen, which may be regarded as in combination with the protoxide of manganese, is evolved in the form of carbonic acid.

Fig. 34.



One equiv. of pure binoxide of manganese = 43.6, yields 2 equivs. = 44 of carbonic acid. So that 0.99 grm. of binoxide of manganese evolves 1.00 grm. of carbonic acid. It is best to employ three times that quantity of the manganese ore, viz: 2.97 grms., which are mixed with a solution of 2.5 grms. of neutral oxalate of potassa; the sulphuric acid is allowed to flow into this mixture, and the amount of carbonic acid evolved is divided by 3. The quotient expresses the percentage of binoxide of manganese contained in the ore.

II. The finely-divided manganese ore is weighed, and mixed with water, in a flask capable of being tightly closed; several bright strips of copper, previously weighed, are then introduced, and a quantity of hydrochloric acid added. The flask is then closed with a cork and narrow tube, and the contents digested until all the manganese has dissolved, care being taken that no chlorine is evolved. The liquid is then heated to ebullition for a quarter of an hour, the flask closed air-tight, and allowed to cool; the solution is poured off, the residual copper washed, first with very dilute hydrochloric acid, then with pure water, dried, and weighed. 2 equivs. of copper = 63.4 parts, require for their conversion into subchloride, 1 equiv. = 71 parts of chlorine.

Then 63.4 : 71 as the amount of copper dissolved is to x (the amount of chlorine sought).

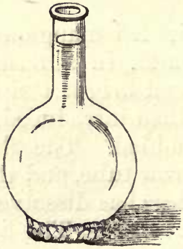
1.22 grms. of pure binoxide of manganese evolve 1.00 grm. of chlorine, and therefore are capable of effecting the solution of 1.78 grms. of copper.

123. CHLORIMETRY.

The "*bleaching powder*" of commerce is a variable mixture of hypochlorite of lime and chloride of calcium, with hydrate of lime. When treated with an acid, it evolves the whole of the chlorine in a free state. In order to determine its value, *i. e.*, the amount of available chlorine which it contains, different methods are employed.

I. Fourteen grms. of pure arsenious acid are dissolved in solution of potassa, and so much water added

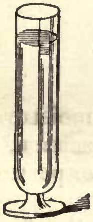
Fig. 35.



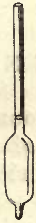
that the liquid may occupy 2000 divisions of the graduated burette. 100 measures, therefore, of this solution contain 0.7 grm. of arsenious acid, and the solution of chlorine which is required to convert this into arsenic acid, contains 0.5 grm. of chlorine, since 1 equiv.=99 of arsenious acid, requires, for its conversion into arsenic acid, 2 equivs.=71 of chlorine.

Five grms. of chloride of lime are weighed off, intimately mixed with water, by trituration, rinsed into a cylindrical (Fig. 36) glass, and so much water added that the whole may occupy 200 measures of the burette.

Figs. 36.

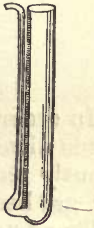


37.



38.

39.



One hundred measures of the arsenic-solution are then, by aid of the pipette (Fig. 37), introduced into a beaker, diluted with water, an excess of hydrochloric acid added, and the liquid coloured with one or two drops of sulph-indigotic acid.

The solution of chloride of lime is well mixed by agitation, introduced into the burette (Fig. 39), and added to the colored arsenic-solution until the color just disappears. The solution of chloride of lime required to produce this effect contains 0.5 grm. of chlorine.

For example, if 90 measures of the solution of chloride of lime had been employed, the 5 grms. of chloride of lime would have contained 1.111 grms. of chlorine, or 22.22 per cent.

Perfectly pure chloride of lime ($Ca\ Cl + CaO,\ ClO$), which is never met with in commerce, contains 48.9 per cent. of available chlorine.

II. A weighed quantity of chloride of lime is mixed with water, in a flask, an excess of protochloride of iron, free from sesquichloride, added, and afterwards some hydrochloric acid. Several bright weighed strips of copper are then introduced, and the solution boiled until the protochloride at first formed is converted into subchloride; the copper is then withdrawn, washed, dried, and weighed. The calculation is effected as in No. 121.

124. ANALYSIS OF NITRE.

In order to determine the amount of moisture in crude nitre, from 5 to 10 grms. of the specimen, previously reduced to powder and dried by exposure to air, are heated to about 150°.

The determination of the quantities of the foreign salts present in the specimen, such as sulphates and chlorides, lime and magnesia, by the ordinary methods, would occupy too much time; it would be preferable to estimate them by means of standard solutions of the reagents, *i. e.*, by measuring the quantities of the latter required to effect complete precipitation.

The appearance of the fracture is regarded as an indication of the quality of the nitre; in pure nitre, the fracture is lustrous, and exhibits a well-defined crystalline appearance; but if not more than 2 per cent. of common salt be present, it is granular and dull. An admixture of nitrate of soda (Chili saltpetre) has the same effect.

Another method, which is likewise, however, inaccurate, but is most readily applied in practice, depends upon the circumstance that a solution of pure nitre, at the temperature at which it is saturated, is still capable of dissolving other salts, especially chloride of sodium. 400 grms. of the powdered specimen are shaken with 500 cub. cents. of a solution of pure nitre; the salt is then filtered off, again washed with 250 cub. cents. of a saturated solution of nitre, dried at 100°, and weighed. The loss of weight expresses the amount of the foreign salts. Since this process is liable to error from many causes, and gives the amount of pure nitre, on an average, 2 per cent. too high, these 2 per cent. must not be neglected in calculating the amount of impurity present.

The following process is more accurate, which consists in converting the nitre contained in any specimen into carbonate of potassa, the amount of which is then determined by means of the standard acid, as in testing potashes.

9.475 grms. of pure nitre furnish a quantity of carbonate potassa, which is capable of saturating 100 measures of the acid mentioned in the testing of potashes; so that if this amount of impure nitre be employed, the number of measures of acid indicate at once the percentage of pure nitrate of potassa in the specimen.

One-fourth of the above quantity (2.369 grms.) of the crude nitre is weighed out, intimately mixed with 1 grm. of ignited lamp-black, or finely pulverized graphite,* and with 12 grms. of ignited and finely-powdered common salt, which serves to moderate the violence of the combustion. The mixture is introduced into a platinum crucible, and heated to redness over a large spirit-lamp or gas-burner. Near the close of the operation a little chlorate of potassa is scattered in the crucible in case the saltpetre happens to contain any sulphates. When cool, it is dissolved in water, and the standard acid added in the manner directed for testing samples of potashes. The number of measures of acid employed is multiplied by 4, in order to obtain the percentage of pure nitre in the specimen.

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* If common coal is used cyanide of potassium and cyanate of potassa may be formed. Pure graphite may be prepared by mixing Ceylon graphite with $\frac{1}{14}$ of chlorate of potassa to which concentrated sulphuric acid is added, and then warmed until no acid fumes are given off. The mass is then shaken with water, the graphite washed and ignited.

In following this method it is impossible to determine the weight of the expelled carbonic acid by means of the apparatus generally employed for this purpose, on account of the large quantity of common salt which has been added.

The simplest method for the analysis of nitre consists in fusing the weighed quantity of nitre with twice its weight of fused bichromate of potassa, until all the nitric acid is driven off. The loss in weight shows the quantity and also amount of pure nitrate of potassa.

125. GUNPOWDER.

I. For the estimation of moisture, 5 or 6 grms. of powder are dried over sulphuric acid, or in the air-bath at 100°.

II. A similar quantity of powder is moistened with water, triturated in a mortar, rinsed into a filter, and thoroughly washed. The solution of nitre thus obtained is evaporated to dryness in a small weighed porcelain dish, the dry residue heated for some time to 200°, or even till the nitre fuses, and its weight determined.

III. In order to determine the sulphur, 5 grms. of powder are intimately mixed with 5 grms. of anhydrous carbonate of soda, 5 grms. of nitre, and 20 grms. of decrepitated chloride of sodium, and the mixture heated to redness in a platinum crucible. When cool, the mass is dissolved in water, the solution slightly acidified with nitric acid, and the sulphuric acid precipitated by chloride of barium. (*See* No. 3.)

The amount of carbon may be inferred by difference. In order to determine its quality, and to ascertain whether it has been completely or incompletely carbonized, the mixture of sulphur and carbon is boiled with a solution of protosulphide of potassium, which dissolves the sulphur, leaving the carbon, which must be well washed and dried. The sulphide of potassium should not contain any free potassa, since this might dissolve an imperfectly carbonized charcoal.—Bisulphide of carbon may also be employed for the extraction of the sulphur.

The sulphur as well as the coal may be completely oxidized by boiling with a solution of permanganate of potassa. The oxide of manganese is afterwards dissolved by hydrochloric acid, and the sulphuric acid precipitated by chloride of barium.

126. HYDROCYANIC ACID.

In order to determine the strength of a solution of pure hydrocyanic acid, a weighed quantity of it is treated with solution of nitrate of silver, which is added gradually, and with frequent agitation, until no further precipitation takes place, and the odor of hydrocyanic acid has entirely disappeared.

The precipitated cyanide of silver is collected upon a filter (previously dried at 120° and weighed), washed, dried at 120°, and its weight determined.

For the estimation of the amount of hydrocyanic acid in the *aqua amygdalarum amararum* and *aqua* *laurocerasi*, they must first be mixed with ammonia, then with nitrate of silver, and lastly with nitric acid.

If hydrochloric acid be contained in the solution, together with hydrocyanic acid, they are both precipitated from a weighed portion of the solution by nitrate of silver, and the precipitate weighed upon a filter dried at 120°. Another weighed portion of the solution is mixed with solution of borax and evaporated to perfect dryness. In this way, all the hydrocyanic acid is volatilized, and the hydrochloric acid converted into chloride of sodium. The dry residue is dissolved in water, the solution acidulated with nitric acid, and the chlorine precipitated by nitrate of silver.

Another method, which may be executed with great rapidity, and suffices for the determination of the hydrocyanic acid in any solution, whether bitter almond-water or laurel-water, &c., or for ascertaining the quantity of cyanogen in crude cyanide of potassium, depends upon the circumstance that 1 equiv. of cyanide of potassium forms, with 1 equiv. of cyanide of silver, a soluble compound which is not decomposed by an excess of alkali, but from which nitrate of silver precipitates the cyanide, or if a little solution of chloride of sodium be previously added, the chloride of silver. The weighed solution, containing hydrocyanic acid is mixed with solution of potassa till it has a strongly alkaline reaction, and a standard solution of silver is then added till a permanent precipitate begins to appear. 1 equiv. of silver employed in the standard solution corresponds exactly to 2 equivs. of hydrocyanic acid.

Ten grms. of pure silver are dissolved in nitric acid, the solution evaporated to perfect dryness, and diluted with so much water, that the whole solution may occupy 1000 cub. cents. 100 cub. cents. of this solution, which contain therefore 1 grm. of silver, represent 0.5 grm. of anhydrous hydrocyanic acid, or 0.481 cyanogen, or 1.206 of cyanide of potassium.

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127. FERROCYANIDE OF POTASSIUM.

$$2\,K\,Cy + Fe\,Cy + 3\,HO = K_2\,Cfy + 3\,HO.$$

The water is determined by heating the finely-powdered salt for some time to about 200°.

The cyanogen can be directly determined only by an organic analysis, *i. e.*, by a combustion.

For the determination of the amount of iron, the salt is intimately mixed with 1½ parts of nitre, and as much carbonate of soda, and the mixture gradually heated to redness in a platinum crucible. On dissolving the fused mass in water, the iron remains behind in the form of sesquioxide, which is washed, ignited, and weighed. Since it is liable to contain a small amount of alkali, it should be dissolved in hydrochloric acid, reprecipitated by ammonia, washed and ignited.

In order to determine the potassium and iron, the salt is dissolved in water, and the solution precipitated by acetate of lead. The precipitate of ferrocyanide of lead is filtered off and washed.

From the solution, which contains all the potassium as acetate of potassa, the excess of lead is precipitated by sulphuretted hydrogen or sulphide of ammonium, the filtered solution evaporated, the residue ignited, the carbonate of potassa converted, by hydrochloric acid, into chloride of potassium, and weighed in that form, after gentle ignition. The ferrocyanide of lead is decomposed by digestion with sulphide of ammonium, the solution of ferrocyanide of ammonium filtered off, evaporated, and the residual mass ignited, with access of air, until only pure sesquioxide of iron is left.

Ferrocyanide of potassium may probably also be decomposed by heating with bisulphate of ammonia. The residue after ignition would then consist of a mixture of sesquioxide of iron and sulphate of potassa, from which the latter might be extracted with water. Or, to insure an accurate result, the ignited residue might be dissolved in hydrochloric acid, the sesquioxide of iron precipitated by ammonia, the solution evaporated, and the residual sulphate of potassa ignited and weighed.

128. EXAMINATION FOR ARSENIC IN CASES OF POISONING.

When poisoning by arsenic is suspected, the poison must be sought in the contents of the stomach and intestines, in the substance of these organs even, and in other entire organs, as the liver, spleen, and lungs; an examination must also be made of the vomited matters, and of the surrounding objects, upon which these may have fallen; the urine and fæces should also be tested for arsenic. The nature of the case will decide in which particular direction the arsenic is to be looked for. It may also sometimes be necessary to examine the remaining portions of suspected food, or the vessels, in which the food has been contained, or even the vessel or paper which may have been used to contain the arsenic. When the body has been long interred, and is far advanced in putrefaction, and the wood of the coffin has rotted away, it becomes necessary to test the surrounding earth for arsenic which may have been derived from the body.

The chemical investigation must be preceded by a very careful examination of the contents of the stomach and intestines, or of the vomited matters. The substances to be examined are spread out in new and clean porcelain dishes, turned over with perfectly clean glass rods or spatulas, and examined with the help of a lens. The analyst should seek especially for small white hard particles or grains of undissolved arsenious acid, which may be carefully picked out with a pair of pincers. These must be looked for especially in the folds of the mucous coat of the stomach and intestines. By stirring up the contents with distilled water, or better, with spirit, and pouring off the lighter organic matters, it is often possible to separate a considerable quantity of the heavy arsenic-powder.

In a judicial investigation of this description, the aim of all chemical operations is to obtain the arsenic in its elementary solid state, as the so-called *metallic arsenic.* In this form alone it is possessed of such highly characteristic properties as to render it impossible to confound it with any other substance, and to allow it to be distinctly recognized even when in almost imponderable quantities. Moreover, all evidence of its presence is insufficient, unless it can be laid before the tribunal in this form; and all other forms and states of combination must be considered as affording inconclusive testimony as to the existence of arsenic in the substance under examination. This preparation or isolation of arsenic in its metallic state, even in the smallest, almost imponderable quantities, is very simple and easy. Great difficulties, however, present themselves, when it is necessary to extract these traces of arsenic, which are diffused through a whole body, from the great mass of organic matter, and to convert them into some form of combination, from which the arsenic can be extracted in the metallic state.

It is most convenient, in considering the process employed for the chemical examination, to regard *three* different cases as possible:—

I. The arsenious acid is found in the solid state in the contents of the stomach and intestines, or in the vomited matters.

II. The poison is intimately and invisibly mixed with, or dissolved in, the contents, &c., and can therefore no longer be found, or separated by mechanical means, in the solid state.

III. The stomach and intestines are empty or no arsenic can be detected in them, since it has already been absorbed into the mass of the blood, or into the substance of the different organs.

I. The arsenic is still to be found in the solid state, and may be picked out or separated by levigation from the contents of the stomach, &c.* This case is the easiest of the three, since it is only to be proved that the substance found is really arsenic. This may be known by the grains or particles exhibiting the following characters, after having been properly freed from organic matter:—

1. The particles are generally milk-white, more rarely clear and semi-transparent, hard, and brittle.

2. A particle of arsenious acid, however small, when introduced into a small tube closed at one end, and heated in the edge of the spirit-flame, volatilizes and recondenses farther up the tube, in the form of a white sublimate which may be seen, especially when examined with a lens, by sunlight, to consist of very lustrous octohedral crystals.

3. A small fragment placed upon red-hot charcoal, is volatilized, emitting a powerful odor of garlic (on red-hot glass or porcelain it volatilizes *without* garlic odor, because it is not reduced to the state of metal).

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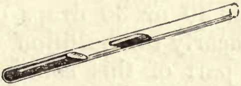
* Poisoning sometimes happens from commercial metallic arsenic (fly-poison, cobalt, &c.). Brownish-black grains or particles should then be looked for, which are easily recognized as arsenic.

4. A particle of the substance is placed in the end of a very narrow tube (Fig. 40), and above it several

Fig. 40.



splinters of freshly-ignited charcoal so that they may occupy about ½ inch of the tube. This part of the tube is now held horizontally, in the flame of the spirit-lamp, in such a manner that the spot where the arsenious acid is placed may remain without the flame. When the charcoal is heated to redness, that portion of the tube is also brought into the flame when the volatilized arsenious acid, passing over the red-hot charcoal, is reduced, and the metallic arsenic deposited beyond the charcoal, in the form of a dark, lustrous, metallic ring. By a gentle heat, this metallic incrustation may be carried still farther up the tube. If the incrustation be chased hither and thither in the tube it is oxidized, or at least partly, and converted into small shining, colorless, volatile crystals of arsenious acid. If the tube be cut off, just before the part which contains the metallic ring, and the latter then gently heated, the characteristic garlic odor of arsenic may be perceived on approaching the nose to the orifice of the tube.

5. This reduction of arsenic to the metallic state may be effected with greater ease and certainty by dissolving a small quantity of the substance in water containing hydrochloric acid, and testing the solution in Marsh's apparatus, in the manner to be presently described more particularly.

6. A particle of the arsenious acid is heated in a small glass tube, closed at one end, with a piece of dry

acetate of potassa about as large as a pin's head, when the indescribably offensive and characteristic odor of kakodyl should be evolved.

7. One or more fragments are finely powdered, under distilled water, the powder rinsed into a small beaker-glass with 20 or 30 drops of water, and the mixture heated nearly to ebullition until the powder is dissolved. A part of this solution is mixed, in a small test-tube, with several drops of solution of nitrate of silver, and afterwards with very dilute ammonia, added drop by drop. In this way, if the substance were arsenious acid, a considerable bright *yellow* precipitate of arsenite of silver will be produced.—Another portion of the liquid, mixed with several drops of a clear solution of ammonio-sulphate of copper, gives a fine *yellowish-green* precipitate of arsenite of copper. A third quantity of the solution, mixed with a few drops of hydrochloric acid, and afterwards with several times its volume of sulphuretted-hydrogen-water, gives a bright *yellow* precipitate of tersulphide of arsenic, which redissolves perfectly on adding ammonia.

Of all these reactions, the reduction to the metallic state in Nos. 4 and 5 is the most necessary, because it is most characteristic and conclusive. The others are to be viewed rather in the light of superfluous confirmations, and are only employed when a considerable quantity of substance is at the analyst's disposal.

II. Arsenic can no longer be perceived by the eye, or mechanically separated, in the solid state, but is contained in a state of solution, or of intimate mixture, in the contents of the stomach, &c. In this case, which is more difficult and of more frequent occurrence than the preceding, the problem consists in dissolving and destroying, by appropriate reagents, the whole mass of the organic matter composing the contents, the vomited matters, the food, and even the stomach and intestines themselves. This is always necessary before the arsenic can be detected with certainty.

It is indispensably necessary that this operation should be preceded by a most careful examination of the reagents to be employed, in order to ascertain whether they contain, as is not unfrequently the case, a small quantity of arsenic. This is equally requisite whether the reagents have been purchased or have been prepared by the analyst himself. The distilled sulphuric acid, the hydrochloric acid, and the zinc must especially be examined. This is most conveniently effected in Marsh's apparatus, which will be presently described, and which is invaluable as allowing the reagents, which are employed in it, to be so readily and surely tested. Without such previous proof of the absence of arsenic in the reagents, upon which the chemist must lay great stress in his depositions, the detection of arsenic in investigations of this description cannot be brought forward in evidence, since it might have been derived from the reagents employed. It should farther be observed and stated in evidence, that the investigation was conducted with new utensils and vessels which had not been used before; and it is advisable, moreover, to insure perfect satisfaction, that it should not be carried out in an ordinary chemical laboratory, or, at all events, that the laboratory should be well cleared before the judicial inquiry is entered upon.

If arsenic should be found in an examination conducted with all these precautions it is still necessary to reflect that it might occur in the body quite accidentally; especially after the administration of certain medicinal remedies, such as the antimonial compounds, preparations of phosphorus, phosphoric, sulphuric, and hydrochloric acids, which may contain arsenic from carelessness in their preparation. Even the hydrated sesquioxide of iron, administered as an antidote in a suspected case of poisoning, might have contained arsenic, unless prepared with great care. Or the arsenic may have been administered as a remedy (especially as a secret medicine). When bodies have been exhumed, it becomes necessary to test the earth with which the coffin has been in contact, since it sometimes happens that soils, especially such as are ferruginous, contain appreciable quantities of arsenic, which might have entered into the body.

Various methods are employed for the modification or destruction of the organic matters, with a view to the extraction of the arsenic.

1. When the substance is in the form of a paste, as in the contents of the stomach and in the fæces, chlorine-gas is passed to saturation. The chlorine is prepared by means of sulphuric acid and manganese, which have been previously tested, and is washed by passing through a small but high column of water. In order to assist the action, the mass may, at the same time, be gently heated. Lastly, when it is completely saturated with gas, coagulated, and bleached, the mixture is heated nearly to ebullition to expel the excess of chlorine, and the solution, which must contain the arsenic, is filtered through paper free from smalt.

2. The stomach and intestines, with their contents, are cut into fine shreds, placed in a porcelain dish, and the whole mass uniformly mixed. About $\frac{1}{3}$ is then set aside in a clean covered glass, in case any accident should happen to the remainder. The mass is then treated with a moderately concentrated solution of potassa, and heat applied until it is entirely or almost entirely dissolved. Only a small quantity of potassa is necessary for this purpose, and the potassa should therefore be gradually added to the mixture, so as to avoid an excess, which would interfere with the subsequent operations. The solution is afterwards slightly

acidified with dilute sulphuric acid, and chlorine-gas is passed, to saturation, into the mass thus coagulated, as in 1.

3. The organic matter cut into shreds, is treated with about as much pure concentrated hydrochloric acid as is equal to the weight of the dry substances contained in the mass; enough water is then added to form a thin paste. The dish is heated on a water-bath, the contents stirred every five minutes, and about 30 grs. of chlorate of potassa (free from lead) added to the hot liquid until it has become clear yellow, homogeneous, and limpid. After being heated for some time longer, the solution is strained through a moistened filter of white paper, free from smalt, the residue washed upon the filter with hot water till the washings are no longer acid, the whole liquid poured together into a porcelain dish, and evaporated to about 1 pound upon the water-bath.

The solution obtained by one of these methods is poured into a cylindrical glass or into a flask, and a slow stream of sulphuretted hydrogen gas passed into it to complete saturation. All the arsenic is thus precipitated as sulphide. Its precipitation is much promoted if the liquid be heated for about half an hour to 50° or 60°, while the gas is passing, and allowed to cool before the stream of gas is discontinued. When saturated, the liquid is allowed to remain for twenty-four hours in a closed vessel. The precipitate which is then deposited has generally, even if much arsenic be present, a dirty, undecided, grayish-brown color.* The greater portion of the solution is poured off, and the precipitate thrown upon the smallest possible filter of Swedish paper, free from smalt, upon which it is well washed. The filtrate, before being thrown away, should, for greater certainty, again be saturated with sulphuretted hydrogen gas and set aside for some time in a closed vessel.

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* If lead, copper, mercury, or antimony were present, the precipitate would also contain the sulphides of these metals, for which it would have to be particularly examined.

This precipitate always contains, in addition to sulphide of arsenic, certain sulphuretted organic matters which are precipitated with it, and must be completely destroyed; this is best effected in the following manner:—

The filter containing the precipitate is placed in a somewhat capacious crucible of genuine porcelain, and digested with concentrated nitric acid until the whole is converted into a homogeneous mass. The free nitric acid, of which more may be added if necessary, is neutralized with pure carbonate of soda, and the solution carefully evaporated to dryness. It is important that the mass should contain a sufficient quantity of nitrate of soda, which is easily insured. It is gradually heated over a large spirit lamp, or gas-burner, until the salt fuses; it blackens at first, but afterwards fuses, quietly and without deflagration, to a clear colorless liquid. The whole of the organic matter is now burnt, and the arsenic converted into arsenate of soda.

Pure concentrated sulphuric acid is then gradually dropped upon the cooled saline mass in the crucible, and a gentle heat applied, until, after addition of an excess of acid, the nitric and nitrous acids are *completely* expelled, and the mass is converted into bisulphate of soda. If nitric acid containing hydrochloric acid had been originally employed for the oxidation of the sulphuretted hydrogen precipitate, a loss of arsenic might now result, from its volatilization as chloride of arsenic. The purity, in this respect, of the nitric acid and carbonate of soda, must therefore have been previously ascertained.

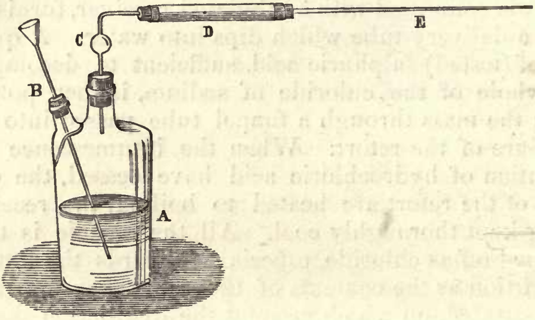
The acid saline mass is now dissolved, in the crucible itself, with the smallest quantity of hot water, and the solution introduced into Marsh's apparatus.

4. The organic matter is introduced, together with the whole of the liquid, into a capacious tubulated retort, and about an equal weight of rock-salt, or of fused common salt, in small fragments, added. The retort is connected with a tubulated receiver, furnished with a delivery-tube which dips into water. A quantity of (tested) sulphuric acid, sufficient to decompose the whole of the chloride of sodium, is then poured upon the mass through a funnel tube passed into the tubulure of the retort. When the intumescence and evolution of hydrochloric acid have ceased, the contents of the retort are heated to boiling, the receiver being kept thoroughly cool. All the arsenic is thus distilled off as chloride, especially towards the last, in proportion as the contents of the retort become more concentrated, on which account the distillation should be carried pretty far. The arsenic is converted into chloride, even when it exists in the mass, in the form of sulphide. The distillate may be at once introduced into Marsh's apparatus. It is safer, since some organic matter might possibly have passed over, to precipitate the arsenic from the solution by sulphuretted hydrogen, and to treat the precipitate as directed above. In the same way the small quantity of arsenic contained in the water in which the hydrochloric acid was condensed, may be precipitated. This method seems to be the most simple and sure, to distil the mass directly with concentrated hydrochloric acid, instead of salt and sulphuric acid, and the arsenic passes over as chloride.

Marsh's apparatus has the following simple construction: *a* is a two-necked bottle capable of holding ½, or at most 1 pint. Both necks are fitted with new perforated corks, which must be perfectly tight. Through one of these, the funnel tube *b* is passed air-tight, and through the other, the bent tube *c*, which is expanded at *c* into a bulb about an inch in diameter.

This bulb serves to collect the particles of liquid which are thrown up from the contents of the bottle, and which drop down again into the latter, from the obliquely cut end of the tube. The other end of this tube is connected, by means of a cork, with the tube *d*, about 6 inches long, which is filled with fused pure chloride of calcium, free from powder, destined to retain the moisture. In the opposite end of the tube *d*, is fixed, air-tight, another tube *e*, made of glass free from lead, 12 inches long, and at most $\frac{1}{12}$ inch in internal diameter. It should be made of rather thick glass, and somewhat drawn out at the end. It must be observed that the funnel-tube *d* is indispensably necessary. If a two-necked bottle cannot be procured, one with a single neck must be provided with a cork bored with two holes.

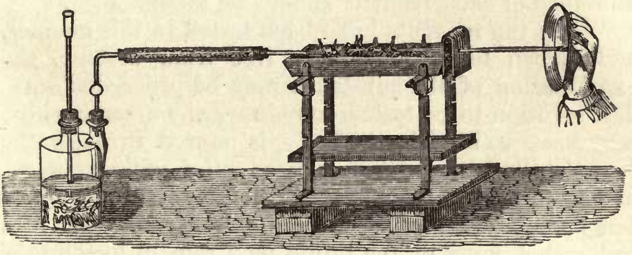
Fig. 41.



A better form of apparatus than the one just described is shown in Fig. 42, which differs from it in having the large tube filled with asbestus to prevent impurities being carried over mechanically by the current of gas.

Several ounces of granulated zinc are introduced into the bottle, which is then half-filled with distilled water: when the apparatus is all arranged, distilled

Fig. 42.



concentrated sulphuric acid is added in small portions by the funnel tube *b*, very gradually, so that the mixture may not become too hot, lest sulphuretted hydrogen should be formed. The evolution of hydrogen is allowed to proceed until it is judged that all atmospheric air is expelled, and that the apparatus is perfectly filled with hydrogen.

The narrow delivery-tube is then heated to redness at *e*, for at least half an hour, by a spirit lamp with a double draught, or a powerful gas-burner, the evolution of hydrogen being constantly maintained by adding acid from time to time. In this way, the acid and zinc are tested for any trace of arsenic which might be present. If they are pure, no incrustation will be deposited at the ignited spot, *e*. If arsenic be present, a metallic mirror is obtained at this portion of the tube, and the acid and zinc cannot be used; even the apparatus must then be carefully cleaned, or, better, replaced by a new one. In the same manner any arsenic might be detected in the hydrochloric acid, the chlorate of potassa (after having been completely converted by fusion into chloride of potassium), the nitre, and the hydrate of potassa (for the third case), which must first be converted into sulphate by adding sulphuric acid. The quantities employed for testing should not be too small; at least an ounce of each reagent should be taken.

When the reagents have been tested in this manner, and shown to be absolutely free from arsenic, the examination of the substance may be proceeded with. The solution to be tested, containing any arsenic which may have existed in the body, is poured through the funnel tube *b* into the apparatus *filled with hydrogen*, and from which hydrogen is being evolved, *the tube e being already heated to redness at the same spot.* In order that none of the liquid may remain in the tube *b*, the latter is rinsed with about the same quantity of pure water, care being taken that no air is poured in with it.

If arsenic be present, there will soon appear, in the portion of the tube *e*, beyond the heated spot, a dark stain, which is at first brownish, and afterwards becomes lustrous and gradually increases until, when large quantities of arsenic are present, it forms an opaque metallic mirror. At the same time the gas issuing from the tube *e* may be kindled, and a dish of white genuine porcelain held in the flame, which should not be too feeble; lustrous black or brownish spots of metallic arsenic will then be deposited, and a great many may sometimes be obtained. When the heated portion of the tube is not very long, more or less arsenetted hydrogen escapes decomposition and furnishes the above-mentioned spots. No imitation of porcelain (stone-ware or delf) should be employed for this purpose, since the glaze of these materials very often contains lead, the reduction of which might produce dark spots even though no arsenic were present. If a large quantity of arsenic be contained in the mixture, so that many thick arsenic-spots can be obtained, they may be easily recognized by means of the characteristic reactions given above, after they have been dissolved in a few drops of nitric acid, and the greater excess of acid has been expelled by a very gentle heat. If only traces of arsenic be present, the spots are so feeble that their nature may remain uncertain. The only indication which is perfectly conclusive, is the production, in the red-hot tube, of a metallic mirror, which must volatilize when gently heated, and re-condense upon a cool part of the tube, at the same time imparting to the evolved gas the peculiar garlic odor.

When the arsenical mirror no longer increases, and the flame ceases to deposit the spots, the operation is discontinued. It is then very convenient to draw the tube *e* gently out, while it is still red-hot and soft, and to close it, when the metallic mirror is obtained in a tube, which may be sealed also at the other end, and laid before the authorities.

If the analyst have reason to believe that a large quantity of arsenic is present, it is well not to employ the whole quantity of liquid at once, but to divide it into several portions, and to make use of a much longer tube *e*, so as to obtain the arsenic-mirror in several places. The tube is then cut with a file into as many pieces as there are mirrors of arsenic. That which contains the most characteristic mirror is sealed at both ends and produced in court; the remaining mirrors are subjected to the tests given at p. 260, among which the ready volatility and alliaceous odor are the most characteristic and decisive.

If after heating the tube for one hour, no stain or mirror make its appearance, and no traces of spots have been obtained from the flame, the absence of arsenic may be inferred, provided that proper care has been taken in the former part of the examination, so that the arsenic cannot have been lost through negligence or awkwardness.

It is very important, in connection with this test (Marsh's) to remember that *antimony* also, whether as teroxide, or as antimonic acid, and especially when in solution in the form of a salt, yields under the same conditions as arsenic, a gaseous antimonetted hydrogen, which deposits upon the heated tube, and upon porcelain, a mirror and spots very similar to those obtained with arsenic. This fact assumes so much greater importance, when it is remembered that preparations of antimony, especially tartar emetic, are administered as internal remedies, so that, in such cases, metallic mirrors are obtained, similar to those of arsenic, but consisting, not of that metal but of antimony. On the other hand, it must not be forgotten that commercial arsenic, as it is employed for poisoning, frequently contains antimony.

If the question be merely whether a metallic mirror consist of arsenic or antimony, it may be readily decided. The arsenic may be easily recognized by the reactions mentioned above, while the antimony-mirror presents very different characters. The antimony-mirror has a lighter color, and is more lustrous than that of arsenic; the antimony spots are darker and have often a tinge of blue. Antimony is not nearly so easily volatilized as arsenic, and although both mirrors may be chased from one part of the tube to another, there is a great difference in the heat necessary in the two cases. A very striking difference between the two deposits is seen in their behavior when heated; the mirror of antimony, before volatilizing, fuses into small lustrous globules, which may, in all cases, be seen with the aid of a lens; the arsenic, however, exhibits no sign of fusion. The most characteristic distinction is the production of the garlic odor when the arsenic is volatilized while the antimony passes off in vapor without any perceptible odor. If that portion of the tube which contains the mirror be heated while the hydrogen is still passing, the gas issuing from the orifice of the tube will have a distinct garlic odor if the deposit consist of arsenic, but will be inodorous if antimony only be present. The following reactions may also be applied to distinguish arsenic and antimony.

The arsenical spots deposited upon porcelain disappear when moistened with a concentrated alkaline solution of hypochlorite of soda; those of antimony, however, are not affected by this reagent. If the spots consist of arsenic and antimony, the latter not exceeding 5 per cent., the spots will also be entirely dissolved. Spots or mirrors of arsenic disappear when moistened with a drop of nitric acid, and gently warmed, forming a clear solution. If a drop of nitrate of silver be added to the solution, and a glass rod moistened with caustic ammonia be held over the liquid, but not allowed to touch it, the mixture assumes a yellow color, from the formation of a precipitate of arsenite of silver. Sometimes, if too strong an acid or too great a heat have been applied, the precipitate consists of reddish-brown *arsenate* of silver. This characteristic color is always produced by nitrate of silver, when the arsenic spots are dissolved by placing the capsule over a vessel containing solution of chloride of lime and sulphuric acid.

It is true that spots and mirrors of antimony also disappear when treated with nitric acid, the antimony, however, is not dissolved, but merely converted into white oxide, which gives no reaction with solution of nitrate of silver. The antimony dissolves in a mixture of one drop of nitric acid and one drop of hydrochloric acid; if the greater excess of acid be carefully evaporated, and sulphuretted hydrogen-water be dropped upon the residue, a fiery-red precipitate of sulphide of antimony is produced. If the spot had consisted of arsenic, a lemon-yellow precipitate would have been obtained.

If the spots be moistened with sulphide of ammonium and dried at a very gentle heat, the arsenic becomes yellow, the antimony orange. The yellow spots of sulphide of arsenic are not affected by hydrochloric acid, while those of sulphide of antimony disappear on gently heating.

If sulphuretted hydrogen gas be passed through the tube containing the metallic mirror, and heat applied, the metal is converted into a sulphide. If the mirror consist of antimony, *black*, or partly *orange-red*, sulphide of antimony is produced, while arsenic gives a *yellow* sulphide. The color, however, is not the only distinction between these compounds, another is afforded by their unequal volatility, sulphide of arsenic being far more volatile than that of antimony.

Moreover, antimony, and arsenic, in the form of sulphides, may be separated by cyanide of potassium, according to the method given in No. 62.

The presence of antimony in the precipitated sulphides may also be ascertained by oxidizing them as directed at p. 266. In that case, the fused mass, before treatment with sulphuric acid, should be dissolved in water, when the antimony would remain undissolved in the form of antimonate of soda.

Or the precipitate by sulphuretted hydrogen may be washed with a concentrated solution of carbonate of ammonia, which is poured over it several times. The sulphide of arsenic is dissolved while the sulphide of antimony remains undissolved. If there is a considerable quantity of the precipitate, a portion may be dissolved in aqua regia, the solution treated with sulphurous acid to reduce the arsenic acid to arsenious, concentrated by evaporation, a piece of bright copper foil placed in it, and then warmed. Antimony and arsenic are reduced and cover the copper with a steel-colored coating, which is easily removed if the copper is heated with caustic ammonia. It is then easily determined which of the metals is present. If both, they may be separated by heating the substance carefully in a slow current of hydrogen. All the arsenic will be sublimed. If hydrogen gas containing arsenic, is passed into a solution of nitrate of silver contained in a Liebig's bulb tube, it forms a precipitate of metallic silver, and arsenious acid, which is easily found in the liquid. Antimonetted hydrogen forms in a solution of silver, a precipitate of antimonide of silver. If a mixture of arsenetted and antimonetted hydrogen from the Marsh apparatus is conducted into a solution of silver, a mixture of antimonide and metallic silver are precipitated. If this precipitate is washed with hot water and then boiled with a concentrated solution of tartaric acid, the antimony alone is dissolved and is then easily recognized by hydrosulphuric acid after acidifying with hydrochloric acid. (*See also* No. 61.)

III. If no arsenic was found in the stomach and intestines, it must be supposed to have been partly carried away in the vomited matters and fæces, and partly absorbed into the mass of the blood, and into those organs which are rich in blood. In this case, the same process is employed as in the preceding, the arsenic being sought, according to the same method, in the liver, spleen, lungs, heart, and kidneys. If urine were found in the bladder, or fæcal matter in the large intestines, they should be examined first. The urine must not be introduced at once into Marsh's apparatus since the frothing to which it gives rise would interfere with the progress of the experiment; the urine should therefore be slightly acidified, with hydrochloric acid, sulphuretted hydrogen passed through it, and the subsequent process conducted as in the second case.

Investigations of this description are in the highest degree laborious, troublesome, and disgusting, when the body to be examined has been interred for months or years, and has passed into a state putrefaction. In such a case, it is frequently no longer possible to distinguish or separate individual organs, and the analyst is then necessitated to examine the whole mass of putrefied organs, or the whole of the soft parts which dry up under some particular local circumstances, and even the bones. When this is the case, the body should not be laid in a bath of chlorine-water or solution of chloride of lime, in order to destroy the offensive odor, since arsenic may thereby be extracted and lost. If chlorine-gas be employed to disinfect the body, it must be evolved by means of distilled sulphuric acid free from arsenic. All the soft parts, especially those which may have formed parts of the abdominal viscera, are carefully separated from the bones, and treated as in the second case.

The following is another convenient process to be especially preferred for the treatment of bodies which have been exhumed entire after some months' interment.

The entire soft parts are treated in a large dish of genuine porcelain, with moderately strong nitric acid, which has been previously tested for arsenic; the dish is then heated upon a sand-bath, and its contents well stirred, until the organic matters are so far destroyed and dissolved as to form a homogeneous pasty mixture. This is now neutralized with a solution of pure hydrate or carbonate of potassa, and about as much finely-powdered nitre (previously tested) added, as is equal in weight to the soft parts. The whole is now evaporated to dryness, with constant stirring, and the dry mass introduced by degrees, in small portions, into a new clean Hessian crucible heated to dull redness. In this manner, the whole of the organic matter is burnt, and the arsenic, if present, converted into arsenate of potassa. In this process, it is important, and not very easy, to add the proper quantity of nitre. If too little nitre be employed, part of the organic matter may remain unburnt, and arsenic may be volatilized from the carbonaceous mass; on the other hand, too much nitre would interfere with the subsequent treatment of the mass. It is better to make a preliminary test with a small portion of the mixture, by introducing it into a small red-hot crucible, and observing whether the mass is perfectly white after deflagration. If it be black and carbonaceous, more nitre must be added.

The mass, which now consists essentially of carbonate, nitrate, and nitrite of potassa, and may also contain arsenate of potassa, is dissolved in the smallest possible quantity of boiling water, and the solution, without filtering off from the suspended phosphate of lime and silica, gradually mixed, in a porcelain dish, with a slight excess of sulphuric acid. The pasty saline mass thus produced is carefully heated till all the nitrous and nitric acids are expelled, a point to which great attention must be paid. On cooling, the mass is stirred up with a little cold water, and the solution poured off from the large deposit of sulphate of potassa. The latter is washed several times with cold water, the washings mixed with the first solution, and the liquid, treated as above, with sulphuretted hydrogen. The precipitate then only requires to be oxidized with nitric acid, with the precaution that the acid must be entirely removed by evaporation before the solution is introduced into Marsh's apparatus.

It is rarely of importance to the evidence that the weight of arsenic existing in a body should be determined. Such an estimation can only be relative, since it is impossible to extract and weigh the *whole* of the arsenic contained in *all* the parts of a body. In such a case, a somewhat longer reduction-tube should be employed, into which is introduced a closely twisted spiral of pure bright copper, about two inches in length; this spiral is accurately weighed with the tube. The latter is then heated in two places, one nearer the evolution-bottle, for the deposition of a mirror; the other, at some distance, where the strip of copper is placed, which combines with all the remaining arsenic, forming steel-gray arsenide of copper. The increase of weight of the tube indicates the amount of arsenic, which is calculated as arsenious acid.

129. EXAMINATION FOR PHOSPHORUS IN CASES OF POISONING.

Since phosphorus has been used to poison mice, &c., and the poisonous action of friction matches has become extensively known, phosphorus has not unfrequently been resorted to as an agent for causing death. It is often necessary, therefore, to examine some article of food, or the contents of a stomach, for this substance. It is obvious that, in cases of the kind, his whole attention must be directed to the separation of the phosphorus in the *free state,* or to producing such reactions as will enable him to infer the presence of *free phosphorus;* since the mere finding of phosphorus in form of phosphates would prove nothing, as phosphates invariably form constituents of animal and vegetable bodies.

A. *Detection of Unoxidized Phosphorus.*

I. Test in the first place the suspected matters as to whether free phosphorus is recognizable by its odor or by its luminosity in the dark, exposing, for this purpose, the materials to the air, as much as is necessary, by rubbing, stirring, or shaking.

II. A portion of the substance is placed, according to the plan of *J. Scherer,* in a small flask; suspend in it, above the substance, by aid of the loosely fitted cork, a slip of filter paper moistened with neutral solution of nitrate of silver, and warm the whole to 85° to 105°

Fah. In case the paper is not colored black after some time, unoxidized phosphorus cannot be present, and it is then unnecessary to proceed further by the methods III. and IV. The operator may go on to (VI.). If, on the other hand, the paper blackens, this is no certain evidence of the presence of phosphorus, because various substances, viz., hydrosulphuric acid (detectable by means of a slip of paper moistened with solution of lead or terchloride of antimony), formic acid, products of putrefaction, &c., may produce the same result. Proceed then with the substance as directed in III. and IV.

III. The luminosity of phosphorus, of all its characters, furnishes the most striking evidence of its presence in the free state. A large sample of the substance is accordingly examined by the following well-proved and admirable method of *E. Mitscherlich.*

Mix the substance under examination with water and some sulphuric acid, and subject the mixture to distillation in a flask, A. (See Fig. 43.) This flask is connected with an evolution-tube *b*, and the latter again with a glass cooling or condensing tube, *c c c*, which passes through a perforated cork, *a*, in the bottom of a cylinder, B, into a glass vessel, C. Cold water runs from D, through a stopcock, into a funnel, *i*, which extends to the bottom of B; the warmed water flows off throuh *g*.*

Now, if the substance in A contains phosphorus, there will appear, in the dark, in the upper part of the condensing tube at the point *r*, where the aqueous vapors, distilling over, enter that part of the tube, a strong luminosity, usually a luminous ring. If you take for distillation 5 oz. of a mixture containing only $\frac{1}{40}$th of a grain of phosphorus, and accordingly only 1 part of phosphorus, in 100,000 parts of mixture, you may distil over 3 oz. of it—which will take at least half an hour—without the luminosity ceasing; *Mitscherlich*, in one of his experiments, stopped the distillation after half an hour, allowed the flask to stand uncorked a fortnight, and then recommenced the distillation: the luminosity was as strong as at first. If the fluid contains substances which prevent the luminosity of phosphorus in general, such as ether, alcohol, or oil

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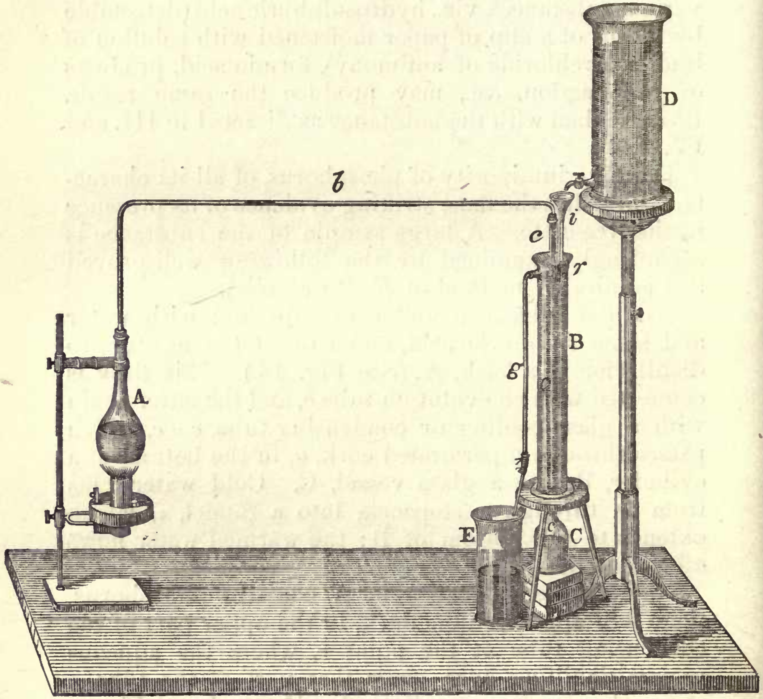
* Instead of this vertical condenser, an ordinary glass one used for distillation may be substituted.

Fig. 43.



of turpentine, no luminosity is observed so long as these substances continue to distil over. In the case of ether and alcohol, however, this is soon effected, and the luminosity accordingly very speedily makes its appearance; but it is different with oil of turpentine which exercises a lasting preventive influence upon the manifestation of this reaction.

a. After the termination of the process, globules of phosphorus are found at the bottom of the receiver, C. *Mitscherlich* obtained from 5 oz. of a mixture containing $\frac{1}{3}$ grain of phosphorus, so many globules of that body that the one-tenth part of them would have been amply sufficient to demonstrate its presence. In medico-legal investigations these globules should first be washed with alcohol and then weighed. A portion may afterwards be subjected to a confirmatory examination, to make quite sure that they really consist of phosphorus: the remainder, together with a portion of the fluid which shows the luminosity upon distillation, should be sent in with the report.

The experiment should be made in a perfectly dark room, best at night. If it is made in the daytime the room should be darkened by aid of curtains or blinds, so that no reflections whatever from the surfaces of the glass vessels or of the fluids moving in them shall occasion mistakes. It is advisable, even, especially when very minute traces of phosphorus are searched for, to pass the evolution-tube through a screen, at *b*, to prevent such reflections being occasioned by the light of the lamp by which the flask is heated.

The residue of the distillation is further examined according to (VI.) for phosphorous acid. The distillate, also, may be tested in the same manner to confirm the presence of phosphorus, or of phosphorous acid arising from its oxidation.

IV. Another sample of the substance may be examined, according to experiments made by *Neubauer* and *Fresenius*, in the following manner. It is brought into a flask with doubly-perforated stopper, water is added, if necessary, and dilute sulphuric acid to aid reaction. Washed carbonic acid gas* is now slowly conducted through the mixture by means of a glass tube passing through the cork and reaching nearly down to the bottom of the flask. From a short tube above the current of gas is led through one or two V-formed tubes which contain neutral solution of nitrate of silver. When the flask is filled with carbonic acid it is warmed in a water-bath. The experiment is kept up for several hours. If free phosphorus be present, a portion of it volatilizes unoxidized in the stream of carbonic acid, and on passing into the silver-solution produces there an insoluble black precipitate of phosphide of silver, together with phosphoric acid. Since a black insoluble precipitate may be caused by various volatile reducing agents or by hydrosulphuric acid, its appearance is not proof of the presence of phosphorus, though its non-formation demonstrates conclusively that free phosphorus is absent.

a. A PRECIPITATE formed in the silver solution in the above experiment is collected on a filter (which has been previously washed with dilute nitric acid and water), and is well washed with water. The phosphide of silver, which may be contained in this precipitate, is detected by the method of *Blondlot*, improved by *Dussard*. *a*, Fig. 44, is an apparatus for evolving hydrogen; *b* is filled with fragments of pumice-stone drenched with concentrated potassa-lye; *c* is a common spring clamp; *d* a clamp that can be nicely adjusted by means of a screw or wedge; *e* is a platinum jet which is kept cool by means of moistened cotton. This platinum jet is essential, since the flame would be colored yellow if burned directly from a glass tube.

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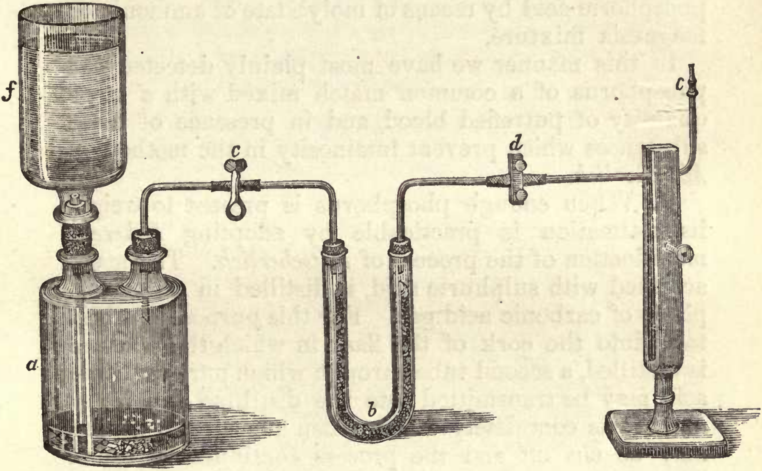
* The apparatus, Fig. 41, may be conveniently employed.

At the outset it is needful to test the sulphuric acid and zinc to demonstrate that they yield hydrogen free from phosphuretted hydrogen. For this purpose allow the gas to evolve until air is displaced from the apparatus, then close *c* until the acid has been forced into *f*, then close *d*, open *c*, and lastly open *d*, cautiously inflaming the gas at the jet and properly regulating its issue. If the flame, when examined in a rather dark place, is colorless, exhibits no trace of a green cone in its interior and no emerald-green tinge when a porcelain dish is depressed into it, the hydrogen is pure. After verifying this result by a second trial, the precipitate to be examined is rinsed into *f*, care being taken that it passes completely into *a*, and the flame is again observed as before. In case but a minimum of phosphide of silver be present the green inner cone and

Fig. 44.



emerald-green coloration of the flame will be perceptible.

b. The SOLUTION filtered from the silver precipitate, is freed from excess of silver by hydrochloric acid, filtered through a well purified filter, strongly concentrated in a porcelain capsule, and finally tested for phosphoric acid by means of molybdate of ammonia or magnesia mixture.

In this manner we have most plainly detected the phosphorus of a common match mixed with a large quantity of putrefied blood, and in presence of those substances which prevent luminosity in the method of *Mitscherlich.*

V. When enough phosphorus is present to weigh, its estimation is practicable by adopting *Scherer's* modification of the process of *Mitscherlich.* The mass, acidified with sulphuric acid, is distilled in an atmosphere of carbonic acid gas. For this purpose it is best to fit into the cork of the flask in which the mixture is distilled, a second tube through which pure carbonic acid may be transmitted into the distilling apparatus, until it is completely filled, when the stream of gas may be cut off and the process continued as usual. The receiver may consist of a flask with a doubly perforated cork, the opening of which passes over the end of the condensing tube, the other carrying a bent glass tube which is connected with a U tube containing solution of nitrate of silver.

When the distillation is finished, globules of phosphorus are found in the receiver, which, after again establishing a gentle stream of carbonic acid, are united by gently heating and then are washed and weighed as described (III. *a.*). The solution poured off from the globules is luminous in the dark, when shaken, though not to the same degree as in *Mitscherlich's* process. The phosphorus in this liquid may be determined, after oxidation, by nitric acid or chlorine, as phosphoric acid; though, only, when the operator is certain that none of the contents of the distilling flask, which usually contain phosphoric acid, have spirted into the condenser. The entire quantity of phosphorus is obtained by adding to that, thus determined, what exists in the U tube. Its contents are treated with nitric acid, the silver thrown down by hydrochloric acid, filtered through a washed filter, concentrated, precipitated as phosphate of ammonia-magnesia, and weighed as phosphate of magnesia.

B. *Detection of Phosphorous Acid.*

VI. In case free phosphorus itself has not been detected by the above methods, it is needful to look for the first product of its oxidation, viz., phosphorous acid. To this end the residue of the distillation (II. *a.*), or (V.), or also the residue of (IV.) is brought into the apparatus, Fig. 44, and tested as described (IV. *a.*) as to any green coloration of the evolved hydrogen. If the phosphorous reaction appears, it is sufficient; otherwise organic matters may have hindered its production. If, therefore, the flame is not colored, the clamp is closed, and a U tube containing neutral solution of nitrate of silver is affixed to the apparatus and the gas is allowed to stream slowly through the silver solution for many hours. In presence of phosphorous acid, phosphide of silver is formed, which is filtered off and examined as directed in (IV. *a.*).

130. SILICATES.*

A few silicates are directly attacked by acids, while others cannot be decomposed by acids, except by the addition of a base, as, for example, lime.

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* **Methods of Sainte-Claire Deville, as given by Messrs. Grandeau and Troost.**

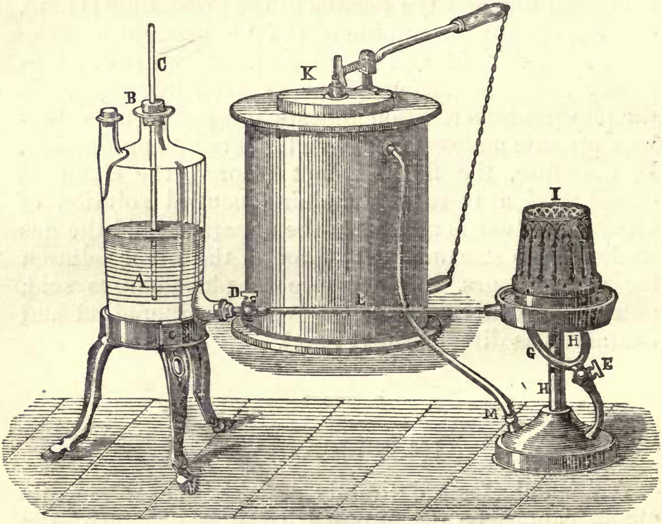
By modifying the composition of a silicate, it may always be rendered decomposable by an acid. For example, a silicate containing the following elements:

Silica,
Alumina,
Iron,
Manganese,
Lime,
Magnesia,
Potassa,
Soda.

This combination occurs in porphyry, gneiss, and granite.

In the first place it is necessary to observe the action of heat upon the silicate, and if there is a loss in weight, to determine its nature, whether it consists of water or fluorine.

Fig. 45.



In most cases, the water contained in a silicate evaporates at a red heat, and it is only necessary to heat it over a lamp fed by bellows. The water from talcose minerals is only driven off at a white heat.

This temperature may be obtained by using the lamp represented in Fig. 43. The apparatus is composed of three principal pieces: a bottle A communicating with the tube E with the reservoir I of spirits of turpentine or the lamp proper, which communicates by the double tube G with an apparatus for the distribution of air forced by the bellows K, which feeds at the same time the tube H.*

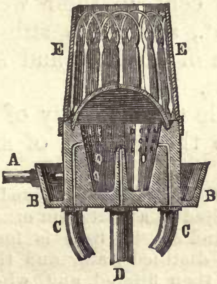
Generally when minerals lose their volatile matter, only at the temperature attained by the large lamp, it is those containing fluorine, and it is then necessary first to examine the nature of the volatile matter.

The calcination is carried on until neither water nor fluorine remains.

It should be noticed whether any material is lost in

*** Fig. 46 shows the interior construction of the lamp. The annular space O O is closed on all parts, above and at the side by**

Fig. 46.



a thick plate; below by a copper plate raised externally in such a manner as to form a little cup around the lamp in which water is poured.

For the management of this lamp we refer to the article by M. H. Deville, Annales de Chimie et de Physique, 3d series, vol. xlvi.

the operations of calcination or not. The substance is introduced in small fragments into a weighed crucible, after which the whole is weighed, then placed over a gas lamp for several minutes, in order to evaporate the water and see if there is any loss indicated by the balance.

It is heated until the weight is constant, and then taken from the smaller lamp and placed over the larger one, Fig. 45; at this temperature it may be fused, decrepitated, change its color, all of which should be carefully noted; when it is certain that the mineral does not lose any more in weight we may proceed to the analysis.

The silicate is decomposed by the means of lime;* there should be the least possible amount of it added, still, it is necessary to employ such a quantity that in pulverizing the glass obtained and treating it with acids the silica will take the gelatinous form.

To decompose bottle glass it is necessary to add from 10 to 20 per cent. of carbonate of lime, window glass a little more of it. Wollastonite, amphibole, and pyroxenes 35 per cent. of their weight; feldspar requires 55 per cent., and some substances containing a large proportion of alumina and silica, as disthene, require 75 per cent.

As a general rule the quantity of lime to be added is in proportion to the amount of silica contained in the substance to be analyzed; the maximum should correspond to the pure silica which requires 110 to 112 per cent.

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* [To prepare it, white marble is dissolved in nitric acid, evaporated to dryness, ignited in a platinum crucible until the nitrate begins to decompose, and caustic lime is formed on the surface. It is then treated with distilled water and the thick liquid boiled for some time. It is then filtered, and, when cold, an excess of concentrated carbonate of ammonia is added. This is decanted and washed for some time with warm water over a funnel covered with a piece of cotton cloth. If there remains any nitrate of ammonia in the carbonate of lime, it will form nitrate of lime during the desiccation or at the commencement of the calcination, and the loss of weight which is thus caused in the carbonate will be an error.]

When an analysis is to be made the quantity of silica is only known approximately by experiments with the blowpipe. With this uncertainty it is better to use too much lime than too little, but a large excess must not be used, for most silicates contain bases somewhat votatile, as potash and soda, which if set free will cause loss.

The silicate is ground, passed through a silk sieve; it is not necessary to carry this sifting very far, at least if the silicate is not very hard or with very great difficulty decomposed, in which case it would be better to pulverize it in a small steel crusher than to employ an agate mortar.

When the steel crusher or mortar is used, it is necessary to digest the powder obtained in nitric acid, wash with water, and ignite gently to bring the material to its original purity; when this is done the substance is placed in the crucible and weighed, and the proper amount of carbonate of lime added.

The mixture being weighed, it should be mixed as thoroughly as possible with a little strip of platinum. All the dust adhering to the platinum should be brushed into the crucible with a small feather, then the feather passed around the interior of the crucible in such a manner as to bring all together at the bottom, and at the same time passed between the crucible and the powder, so as to detect the mixture.

During this time the powder has absorbed a little moisture; the crucible is placed for a moment over the small lamp* and heated to such a temperature that each part of the surface of the matter becomes incandescent, allowed to cool, again weighed, and a difference is always found, provided the carbonate contains hygroscopic water.

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* Ordinary gas lamp without bellows. The lamp with turpentine and bellows is termed the larger, and the gas lamp with only bellows attached, the smaller.

The material being thus prepared, it is heated for fifteen or twenty minutes over the smaller lamp (gas lamp fed by bellows) in such a manner that the carbonate acts upon the silicate without fusing; after having thus expelled the carbonic acid, the substance is placed over the large lamp, and it is necessary that the glass produced should be well fused, homogeneous, and if it is colored, transparent; all the peculiarities should be observed, and the weight thus produced should be determined.

The glass should then be detached from the crucible with the greatest possible care, in such a manner as not to lose any of it, placed in an agate mortar, covered with sheepskin, and ground with care, but not too fine. The pulverized glass is then placed in a weighed platinum crucible, heated to 200° or 300°, and the glass to be analyzed weighed.

The glassy material moistened with water is treated with nitric acid, being stirred constantly with a glass rod, so as to prevent the mixture forming a compact mass at the bottom of the crucible. When all that is found upon the glass rod is detached, and it is heated over the lamp to be sure that nothing remains, the crucible is placed upon the sand-bath and heated to such a temperature that no more nitric acid is given off and nitrous vapors begin to form.

If the material contains any iron or manganese, it is necessary to wait until the color becomes uniformly red or black, and then there should be added enough of a concentrated solution of nitrate of ammonia to moisten the entire mass, which is heated over the sand-bath, covering the crucible with a funnel; after a moment it is uncovered and odor observed. If the smell of ammonia is distinctly perceived, the process is continued; if it is not, a drop of ammonia is added with a glass rod, the mixture stirred, and notice is taken if the smell of ammonia remains and if a precipitate is formed; generally there is no precipitate, and it is then certain that all the alumina has been precipitated by the calcination. It is left to digest on the sand-bath until it is also certain that the nitrate of ammonia has penetrated the whole mass, then a little water is added, and the liquid decanted, to prevent accident, on a filter.

Water is again placed in the capsule, boiled, decanted, and washed a dozen times in order to be sure that the boiling water penetrated the entire mass; when the decanted liquid leaves no residue if evaporated on platinum foil, the washing is discontinued.

The material submitted to analysis is then divided into two portions—first, the portion soluble in nitrate of ammonia, and secondly, the insoluble portion left in the capsule.

The insoluble portion in the capsule is treated with nitric acid, whic his left to digest slightly heated; nitric acid dissolves the alumina and the peroxide of iron.

If manganese is not present, the silica which remains is white; if present, it is black. The silica is washed, and the washings evaporated in a platinum crucible and ignited.

The mixture of alumina and oxide of iron is weighed.

If the silica contains peroxide of manganese, it is washed with dilute sulphuric acid, adding a crystal of oxalic acid. The oxalic acid decomposes the binoxide of manganese and converts it into peroxide, which dissolves in sulphuric acid; the sulphate of manganese is washed; the sulphate mixed with sulphuric acid in a platinum crucible is heated to 300° to 400°, and the sulphate of manganese weighed; the silica remains in a state of purity after all these treatments and washings, as much in the capsule as upon the filter, which is used for decantations. All these decantations should be made upon the same filter.

The filter is again placed over the silica in the capsule, the whole gently dried upon the sand-bath, then moderately calcined, when the silica should become white.

The crucible and its cover are placed upon the balance, and quickly weighed. Inasmuch as the crucible cools, the weight that it is necessary to place on the side of the silica to obtain an equilibrium diminishes more and more, by reason of the cooling of the surrounding air; on the other hand, as this cooling takes place, the silica absorbs the moisture to such an extent that its weight is changed and augmented even so as to be seen.

The crucible is then placed again warm upon the balance, the weights taken away from the side where the silica is, until the increase of weight of the silica ceases to be rapid. At the moment the balance is at rest, the weight is noted, which gives the weight of the silica.

At this point in the analysis the weight has been found; first of the silica, secondly of the mixture of alumina and iron containing a little manganese.

To be sure that the silica is pure, it is dissolved in very dilute hydrofluoric acid; if quite pure it will leave no perceptible residue, except the ash of the filter. It is evaporated with a little sulphuric acid, and should leave no residue.

After having weighed the crucible which contains the material after the ignition of the alumina and iron, the mixture is carefully removed and placed in a small platinum boat, previously weighed in a small corked tube; the boat is heated to redness, and again weighed with its case or tube. The boat is then introduced into a platinum or porcelain tube, by aid of a small wire which conducts the boat to the part of the tube, where it should be heated. The tube is then heated to redness and a current of hydrogen passed through it.* When the iron is reduced, the stream of hydrogen is replaced by a current of hydrochloric acid gas, which is continued for an hour or two. Fig. 48 shows the arrangement of this part of the analysis. There may be placed at the extremity of the tube a small flask, in which all volatile materials will condense if any escape from the tube. When the current of hydrochloric acid

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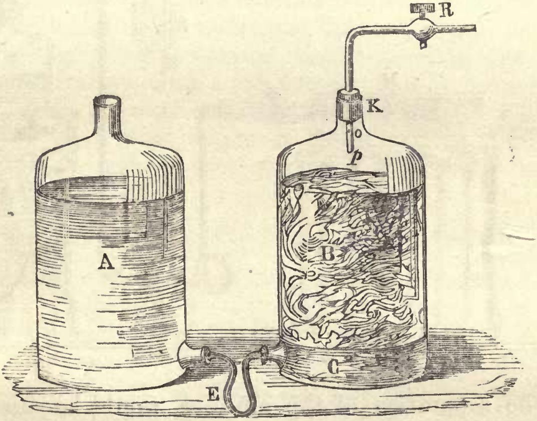
* Fig. 47 represents a convenient apparatus for hydrogen.

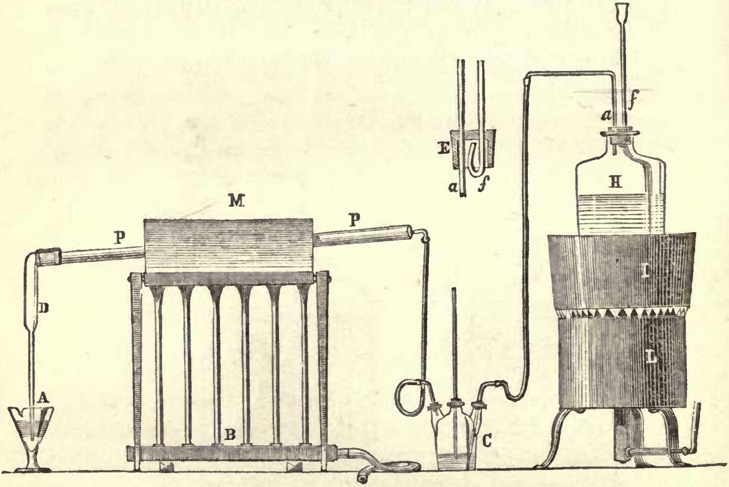
Fig. 47.



A and B are two bottles of four or five litres capacity, and tubulated at the bottom. By means of a rubber tube E they are united in such a way as to put them in communication. The mouth of the bottle B is closed by a cork, which is pierced by a glass tube terminated with the stopcock R. The bottle B is filled with fragments of glass to the level of the smaller tube, and a larger part of the space above with zinc. The bottle A is filled with water and hydrochloric acid. By opening the stopcock R, the acidulated water passes to the zinc, and the hydrogen is only given off when the gas is used.

has passed long enough, which may be known by its producing no more protochloride of iron, it is stopped, the hydrogen again passed to expel the vapor of hydrochloric acid, and the tube left to cool before taking the boat from it. This is placed again in the case or tube and weighed; the weight it has gained gives the weight of the alumina.

Fig. 48.



The separation of the alumina would be complete if the mass was perfectly pure, which is not the case, if the material which comes from the nitrates is not sufficiently washed.

In this case, the material which has been treated with nitric acid, then with hydrochloric acid, may contain lime left with the alumina. The lime is found as chloride of calcium. The alumina is moistened with a small quantity of water, which is decanted, washed several times, dried, ignited in the boat, and weighed in the glass tube. There should be no change of weight, and a drop of oxalate of ammonia should give no precipitate in the washings if the alumina was pure. In the case of a precipitate a diminution of weight in the alumina would be found at the same time. The alumina is washed, dried, and weighed. The last weight obtained is taken for the definite weight of the alumina, and the difference from the first weight divided by two gives the weight of the lime ($CaO = 28$, $CaCl = 56$).

To verify this weight, all the lime contained in the washings is precipitated by oxalate of ammonia, ignited, weighed, and this gives directly the weight of the lime.

To determine by difference the quantity of iron and manganese which exists in the material at the same time with the alumina, we take from the entire quantity used for analysis: 1st, the weight of the pure alumina; 2d, the weight of the lime; the difference gives the weight of the mixture of iron and manganese.

Separation of the Iron and Manganese.

If the substance does not contain manganese, or if it is not necessary to determine the manganese separately, the analysis of the material insoluble in nitrate of ammonia is finished. But if the iron and the manganese are to be separated, recourse may be had to the following method:—

Into a platinum tube a current of vapor of water, furnished by a retort containing distilled water and a few drops of hydrochloric acid, is passed. This vapor will be condensed in the tube, and will take with it into the flask or globe all the chloride of iron and manganese produced by the evaporation. This washing done, the waters are placed in a small crucible, and a few drops of sulphuric acid added, evaporated to dryness, and the sulphates gently calcined until the weight is constant; the mixture of sesquioxide of iron and sulphate of manganese is then weighed, a little water poured upon the sulphate, decanted and washed upon a filter, which is ignited with the peroxide of iron and weighed. This weight is the oxide of iron, which, taken from the weight previously obtained, gives that of the sulphate of manganese. By adding the red oxide of manganese deducted from the weight of the sulphate with the oxide of iron, the exact total weight of manganese and iron is known, which have been calculated by difference at the time when the pure alumina was weighed. This verification dispenses with the direct weight of the sulphate of manganese. If, however, it is deemed desirable to determine it, the sulphate from the washing should be evaporated, and the manganese may be weighed in this form.

The preceding operations may be verified in the following manner:—

1st. The alumina should be colored or slightly tinged with gray; it should be soluble in bisulphate of potassa in large excess.

2d. The oxide of iron, tested with the blowpipe with carbonate of soda in the oxidizing flame, should give no green color.

3d. The sulphate of manganese, treated with the sulphate of ammonia, a little nitric acid and ammonia, should give no precipitate.

Analysis of the Materials soluble in Nitrate of Ammonia.

They contain 1st, lime; 2d, magnesia, and sometimes manganese; 3d, potassa, 4th, soda.

The liquid contains at first a certain quantity of lime, which has been introduced to decompose the mineral. A quantity of pure crystallized oxalate of ammonia should be weighed out, sufficient to precipitate more than the quantity of lime present. It suffices for this purpose to multiply the weight of the lime by 2½ and to place this weight of pure pulverized oxalate in the liquid which is stirred and left to settle. When the liquid is clear, there should be added two or three drops of oxalate of ammonia, and if there is a precipitate, it is certain there was lime in the material to be analyzed. There is added, successively and in quantities estimated approximately, solid oxalate of ammonia and a few drops of the dissolved oxalate, in such a manner as to be sure to have an excess of oxalate of ammonia and to add the least possible quantity of the solution of the oxalate so as not to increase the quantity of the liquid. It is left to settle for eight or ten hours and then decanted upon a filter. All the oxalate of lime is placed on the filter, by washing it little by little with warm water. The precipitate is then dried, ignited a sufficient number of times, and weighed. This determines the weight of the lime. From this weight increased by that which has already been found, the weight of the lime added to decompose the mineral is subtracted. This gives the weight of the lime existing in the original substance.

The liquid which remains is evaporated in a platinum capsule, until the fluid is concentrated and syrupy. It contains considerable nitrate of ammonia, a little oxalate of ammonia, and nitrates of magnesia, manganese, potassa, and soda. It is covered with a glass in such a way as to transform the capsule into a closed vessel, and the saline mixture is heated. The nitrate of ammonia is converted into nitrous oxide, the oxalate is decomposed and volatilized, and there remains in the capsule and on the glass those substances which it is necessary to heat to 300° with the gas or alcohol lamp. 1st, nitrates and subnitrates of magnesia and manganese; 2d, nitrate of potassa; 3d, nitrate of soda.

A little water is added and a trace of pure tartaric acid, which being evaporated to dryness is disengaged with the vapors of nitric acid. The interior of the capsule will be filled with beautiful crystals of volatilized oxalic acid; it is heated to dull redness by covering the capsule in such a way that the carbonic acid may not be burned in the interior. In this operation the oxalic acid has driven off the nitric acid and changed the nitrates into oxalates; these at a red heat are converted into carbonates, and if by chance a small quantity of nitrate has escaped during the reduction, the carbonic oxide and tartaric acid would have eliminated it, so that there would remain only carbonates.

Water is now added to the magnesia and manganese remaining in the capsules, and the alkaline carbonates are dissolved. It is decanted upon a very small filter, because it is not necessary to wash the carbonate of magnesia much; it is remarkably soluble, particularly in cold water, and therefore the washing water should be boiling hot when used.

The mixture of carbonate of magnesia and manganese is heated to redness and thus converted into magnesia and red oxide. The mixture is weighed in the same capsule in which the evaporation has been made. It is then treated with a boiling concentrated solution of nitrate of ammonia, and heated until no more ammoniacal fumes are given off. It is decanted, and the insoluble material washed, if any exists, and should be of a brown color. The capsule is then heated to redness and weighed. The difference between these two weights gives the magnesia, and what remains in the capsule gives the weight of the manganese, the ammoniacal fluid containing the magnesia is placed aside to be examined as directed hereafter.

The soluble carbonates of soda and potassa are treated with hydrochloric acid for experiment in a glass closed with a stopper. This glass is put in a warm place for ten or twelve hours, so that all evolution of the hydrochloric acid may cease in the liquid; the stopper is washed, the liquid in the glass evaporated, and the washing waters are also evaporated in a platinum crucible; the water and excess of hydrochloric acid are driven off, and a mixture of chloride of potassium and sodium is obtained, which always crystallizes in cubes when the chloride of sodium is in excess. Sometimes these chlorides have a slight red color, caused by a small quantity of nitrate left in the carbonates, but any error is prevented by heating the chlorides to such a temperature as to decompose the chloride of platinum formed. The chlorides become black by the presence of the platinum, but this metal from the vessels does not alter the weight of the chlorides.

The alkaline chlorides being weighed, a small quantity of water is added, and some chloride of platinum, if there is any potassa. The mixture of chloride of platinum and alkaline salts is evaporated to a syrupy consistency, and treated with pure alcohol. The residue consists of the double chloride of platinum and potassium, and some chloride of sodium. It is dried and calcined in order to reduce the platinum. The chlorides of potassium and sodium are separated by water; the mixture is again ignited and weighed. The material which remained in the crucible is the platinum which proceeds from the double chloride. From the weight obtained we deduct that of the chloride of potassium which it contains; by subtracting from the weight of the alkaline chlorides the weight of the chloride of potassium, the weight of the chloride of sodium is obtained. Having these weights it is easy to determine that of the potassa and soda.

The following verifications may then be made: 1st. The lime which has been heated till cessation of loss of weight should be soluble in nitrate of ammonia, with no other residue but the ashes of the filter. 2d. By adding ammonia-phosphate of soda to the ammoniacal solution of magnesia, the bulky precipitate of phosphate of ammonia and magnesia is formed. 3d. The manganese is verified as above stated. 4th. The chlorides of sodium and potassium are evaporated, gently ignited, and when treated with a mixture of alcohol and ether should not give any substance capable of coloring the flame red, which would indicate the presence of lithia.

The materials which are decomposed by acids are treated directly in the same manner as those that are rendered decomposable by lime; but it is necessary to do this in such a manner that the silica is always separated in a gelatinous mass. If not, it is necessary to ignite it with lime to bring it into this state. Thus our condition is that the substance can be decomposed by acid, producing gelatinous silica. The glass resulting from the decomposition of the mineral by lime, should have for its weight the sum of the weights of the materials used, and the lime added. The difference should be one milligramme, or two milligrammes at most; it is more frequently nothing.

Examination of the volatile materials in silicates.

It has been seen at the commencement of the analysis of the silicates that it is necessary to heat the substance to a very high temperature to expel the volatile materials. The water is freed at the temperature obtained by the small lamp; but when it is necessary to use the large lamp, the presence of fluorides is indicated.

The better way to make the presence of water in a mineral evident, is to place the material in a platinum tube, and pass a current of dry gas through the tube at a red heat; a tube containing chloride of calcium is arranged to receive the water. This method is not always adopted, because it is frequently possible to determine other things with the water, but is sometimes useful. In case there is only water, as in the zeolite, the ignition and loss of weight indicate the amount of water.

When there is any evolution of volatile materials at a high temperature, these are, as stated, fluorides. There are a large number of fluorides, but we shall consider only those which may be expelled by calcination; the fluoride of silicium, the fluoride of boron, and the alkaline fluorides.

All the fluosilicates may be decomposed by heat, and all the fluorides, mixed with a sufficient quantity of silica, are changed into fluoride of silicium; therefore the fluoride of silicium may be determined at once, and it will be easy to determine the other fluorides.

When a substance contains fluoride of silicium in a large quantity, topaz for example, and when it is desirable to collect and determine this fluoride, the following method may be used: take three platinum crucibles, a large, medium, and small one. In the small one, which has been weighed, the material to be ignited is placed and weighed; over the small crucible, covered with its lid, the medium crucible is inverted so as to form a cap, and finally the two crucibles thus arranged are placed in the large crucible; the whole are weighed together in such a way that the weight of the apparatus, less that of the topaz, may be ascertained. Then pour between the last two crucibles a certain quantity of carbonate of lime and weigh it. This gives the weight of the apparatus, the topaz, and the carbonate of lime.

The whole is heated to a red heat, the carbonate of lime is reduced to quicklime, and it is heated for a long time over the large lamp until the fluoride of silicium is completely expelled. When it is certain that the loss of the topaz is terminated, the crucible is taken from the fire and weighed; there should be no loss except of the carbonic acid of the lime and the water. The quantity of the carbonate of lime being known, and therefore that of carbonic acid, it follows that the loss of weight, that of the carbonic acid being deducted, depends entirely upon the quantity of water which may have passed through the lime without being absorbed.

This done, the crucible is slightly inclined, the lime taken out with the greatest care, generally rendered compact and adhering to the crucible by the presence of the fluoride of calcium and the silicate of lime. When a sufficient quantity of lime has been taken out to free the medium crucible, this is withdrawn, and then the interior crucible is free; it is weighed, and the loss of weight gives the fluoride of silicium which is evolved.

It is necessary to prove that this is fluoride of silicium. The composition of fluoride of silicium is SiF_3; if it is passed through the lime, it forms $SiO_2,CaO+3CaF$, a mixture of fluoride of calcium and silicate of lime, which gives an excess of lime again. It is necessary to take all the substance around the medium crucible into the large crucible and boil it with nitrate of ammonia, which does not decompose the fluoride of calcium and silicate of lime. The quicklime is thus disposed of, and fluoride of calcium and silicate of lime remain in the proportions indicated above $SiO_2CaO+CaF$.

The substance treated with sulphuric acid should be completely converted into sulphate of lime and fluoride of silicium. Therefore, after having treated it with nitrate of ammonia and washed it, sulphuric acid is added until no vapors are given off; the sulphate of lime thus formed is treated with boiling water and acid until wholly dissolved. This washing is done on a filter, so that the sulphate may be acted upon more readily by the hot water. The residue on the filter is ignited, and should consist of only a very small quantity of silica.

Fluoride of silicium and fluorine may be in excess, so that it may be possible to suppose an expulsion of free fluorine and fluoride of silicium. But this is not probable, because generally the silica is in excess of the fluorine, and cannot be set free without combining with the silica; the topaz containing a large quantity of fluorine, and but little silica, only sets free fluoride of silicium. Admitting, however, that an excess of fluorine may exist, it is at the same time supposed that it contains no water.

A sufficient quantity of silica is added so that only fluoride of silicium will be set free, and two estimates are made; in the first the material alone is determined, and in the second the loss of the substance to which the silica has been added. The difference gives the amount of silicium necessary to neutralize the fluorine, and the quantity of free fluorine existing in the materials is deducted from it.

EQUIVALENT WEIGHTS OF THE ELEMENTS.

		H=1.
Aluminum	Al	13.7
Antimony	Sb	122
Arsenic	As	75
Barium	Ba	68.5
Bismuth	Bi	208
Boron	B	11
Bromine	Br	80
Cadmium	Cd	56
Cæsium	Cæ	133
Calcium	Ca	20
Carbon	C	6
Cerium	Ce	46
Chlorine	Cl	35.5
Chromium	Cr	26.24
Cobalt	Co	29.5
Columbium	Cb	47
Copper	Cu	31.7
Didymium	D	48
Erbium	E	56.3
Fluorine	F	19
Glucinum	G	9.3
Gold	Au	196.6
Hydrogen	H	1
Indium	In	35.9
Iodine	I	127
Iridium	Ir	99
Iron	Fe	28
Lanthanum	La	46.4

		H = 1.
Lead	Pb	103.5
Lithium	Li	7
Magnesium	Mg	12
Manganese	Mn	27.5
Mercury	Hg	100
Molybdenum	Mo	48
Nickel	Ni	29.5
Nitrogen	N	14
Osmium	Os	99.6
Oxygen	O	8
Palladium	Pd	53.3
Phosphorus	P	31
Platinum	Pt	98.7
Potassium	K	39.1
Rhodium	Rh	52.2
Rubidium	Rb	85.4
Ruthenium	Ru	52.2
Selenium	Se	39.7
Silicium	Si	14
Silver	Ag	108
Sodium	Na	23
Strontium	Sr	43.75
Sulphur	S	16
Tantalum	Ta	91
Tellurium	Te	64
Thallium	Tl	204
Thorium	Th	115.7
Tin	Sn	59
Titanium	Ti	25
Tungsten	W	92
Uranium	U	60
Vanadium	V	51.3
Yttrium	Y	30.9
Zinc	Zn	32.6
Zirconium	Zr	44.8

EQUIVALENT WEIGHTS OF COMPOUND BODIES.

$H = 1.$

		$H = 1.$
Alum	$\left\{\begin{matrix} KO, SO_3, Al_2O_3, \\ 3SO_3 + 24HO \end{matrix}\right\}$	474.6
Alumina	Al_2O_3	78.8
Ammonia	NH_3	17
——— carbonate of	$2NH_4O, 3CO_2$	118
Ammonium	NH_4	18
——— chloride of	NH_4Cl	53.5
——— oxide of	NH_4O	26
——— platinochloride of	$NH_4Cl, PtCl_2$	223.2
Antimonious acid	SbO_3	153
Arsenate of magnesia-ammonia	$2MgO, NH_4O, AsO_5 + HO$	190
Arsenic acid	AsO_5	115
Arsenious acid	AsO_3	99
Barium, chloride of	$BaCl$	104
——— silicofluoride of	$3BaF, 2SiF_3$	419.1
Baryta	BaO	76.5
——— carbonate of	BaO, CO_2	98.5
——— chromate of	BaO, CrO_3	127.3
Berylla (glucina)	Be_2O_3	52.2
Biborate of soda	$NaO, 2BO_3 + 10HO$	190.8
Binoxalate of potassa	$KO, 2C_2O_3 + 3HO$	146.2
Bismuth, teroxide of	BiO_3	232
Bitartrate of potassa	$KO, HO \bar{T}$	188.2
Cadmium, oxide of	CdO	64
Calcium, chloride of	$CaCl$	55.5
Carbonic acid	CO_2	22
Chromate of lead	PbO, CrO_3	162.4
Chromic acid	CrO_3	50.7
Chromium, sesquioxide of	Cr_2O_3	77.4
Cobalt, protoxide of	CoO	37.5
Copper, protoxide of	CuO	39.7
——— suboxide of	Cu_2O	71.4
Cyanide of silver	$AgCy$	134
Cyanogen	$C_2N = Cy$	26
Ferrocyanide of potassium	$2KCy, FeCy = K_2Cfy$	184.4

		H = 1.
Ferrocyanide of potassium containing water of crystallization	$\left\{ \begin{matrix} 2KCy, FeCy+3HO \\ =K_2Cfy+3HO \end{matrix} \right\}$	211.4
Fluoride of calcium . . .	CaF	39
Hydrochloric acid . . .	HCl	36.5
Iodide of palladium . . .	PdI	180.4
—— of potassium . . .	KI	166.3
Iron, protoxide of . . .	FeO	36
—— sesquioxide of . . .	Fe_2O_8	80
Lead, acetate of . . .	$PbO, \bar{A}+3HO$	189.5
—— chloride of . . .	$PbCl$	139.2
—— protoxide of . . .	PbO	111.7
—— red oxide of . . .	PbO, Pb_2O_3	342.5
Lime	CaO	28
—— carbonate of . . .	CaO, CO_2	50
Magnesia	MgO	20
Manganese, peroxide of . .	MnO_2	43.6
———— protosesquioxide of .	MnO, Mn_2O_3	114.8
———— protoxide of . .	MnO	35.6
Mercury, protochloride of . .	$HgCl$	135.5
——— protoxide of . . .	HgO	108
——— subchloride of . .	Hg_2Cl	235.5
——— suboxide of . . .	Hg_2O	208
Molybdenum, binoxide of . .	MoO_2	62
Molybdic acid	MoO_3	70
Nickel, protoxide of . . .	NiO	37.6
Nitrate of baryta . . .	BaO, NO_5	130.5
——— of lead	PbO, NO_5	165.7
——— of potassa . . .	KO, NO_5	101.2
——— of silver . . .	AgO, NO_5	170.1
——— of soda	NaO, NO_5	85
——— of strontia . . .	SrO, NO_5	105.8
Nitric acid	NO_5	54
———— hydrated . . .	HO, NO_5	63
Oxalic acid	C_2O_3	36
———— hydrated . . .	$3HO, C_2O_3$	63
[a]Phosphate of magnesia . .	$2MgO, PO_5$	111
[b]———— of soda . . .	$2NaO, PO_5$	133
[b]———— of soda with water of crystallization . . .	$2NaO, HO, PO_5+24HO$	358
Phosphoric acid . . .	PO_5	71
Potassa	KO	47.2
——— bichromate of . .	$KO, 2CrO_3$	148.6
——— carbonate of . . .	KO, CO_2	69.2
——— chlorate of . . .	KO, ClO_5	122.7
——— chromate of . . .	KO, CrO_3	97.9
——— hydrate of . . .	KO, HO	56.2
Potassium, chloride of . .	KCl	74.7

		H = 1.
Potassium, platino-chloride of	$KCl, PtCl_2$	244.4
Silicic acid	SiO_2	30
Silicium, terfluoride of	SiF_3	71
Silver, chloride of	$AgCl$	143.6
—— oxide of	AgO	116.1
Soda	NaO	31
—— carbonate of	NaO,CO_2	53
—— carbonate of, containing water of crystallization	NaO, CO_2+10HO	143
—— hydrate of	NaO, HO	40
Sodium, chloride of	$NaCl$	58.5
Stannic acid	SnO_2	74
Strontia	SrO	51.8
Sulphate of ammonia	NH_4O, SO_3+HO	75
———— of baryta	BaO, SO_3	116.6
———— of copper	CuO, SO_3+5HO	124.7
———— of lead	PbO, SO_3	151.5
———— of lime	CaO, SO_3	68
———— of potassa	KO, SO_3	87.2
———— of protoxide of iron	FeO, SO_3+7HO	139
———— of soda	NaO, SO	71
———— of strontia	SrO, SO_2	91.8
Sulphide of antimony	SbS_3	177
———— of arsenic	AsS_3	123
———— of copper	CuS	47.7
———— of lead	PbS	119.7
———— of mercury	HgS	116.0
———— of molybdenum	MoS_2	78.0
———— of silver	AgS	124.1
———— of zinc	ZnS	48.6
Sulphuretted hydrogen	HS	17
Sulphuric acid	SO_3	40
———— (hydrated)	HO, SO_3	49
Sulphurous acid	SO_2	32
Tin, protoxide of	SnO	66
Titanic acid	TiO_2	41
Tungstic acid	WO_3	116
Water	HO	9
Zinc, oxide of	ZnO	40.6

ERRATUM.

Page 287, 4th line from top *for* Fig. 43 *read* Fig. 45.

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